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UTILIZATION OF TEXAS SERPENTINE

By

VIRGIL E. BARNES, D. A. SHOCK, AND
W. A. CUNNINGHAM



Bureau of Economic Geology

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The benefits of education and of useful knowledge, generally diffused through a community, are essential to the preservation of a free government.

Sam Houston

Cultivated mind is the guardian genius of Democracy, and while guided and controlled by virtue, the noblest attribute of man. It is the only dictator that freemen acknowledge, and the only security which freemen desire.

Mirabeau B. Lamar

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UTILIZATION OF TEXAS SERPENTINE

Virgil E. Barnes, D. A. Shock, and W. A. Cunningham

ABSTRACT

The serpentine deposits of the Llano uplift are reviewed in Part 1 of this paper with their utilization as outlined in Part 4 in mind. It is concluded that the most significant deposit is the Coal Creek deposit in Gillespie and Blanco counties, where about 11 billion short tons of serpentine exist, of which a billion tons could be quarried easily. In comparison the rest of the deposits are small with seldom more than a quarter million tons of recoverable serpentine being present in any one deposit, or more than a million tons in any one area. Many of the smaller deposits are irregular in shape and contain an excessive amount of inclusions which would make quarrying them expensive.

The mineral and chemical composition and the crystal structure of the serpentine minerals are discussed in Part 2. Attention is focused on crystal structure with the hope that it will furnish some explanation of those things which happen upon chemical and physical treatment of the serpentine, and that future experiments of value will be suggested.

Experimental data on the utilization of Coal Creek serpentine are contained in Part 3. Heat treatment was used to make the serpentine more reactive, and the best

range of temperature, time, and particle size to use is outlined. Thermal analyses curves were run, and X-ray diffraction patterns were made of the serpentine during various stages of heating. Experiments on the treatment of raw and activated serpentine with hydrochloric acid and of activated serpentine with magnesium sulfate solutions are described. The solubility in sodium hydroxide of the silica residue from the hydrochloric acid extraction was determined; and the effect of the silica-soda ratio, the effect of the concentration of soda, and the effect of the particle size on solubility were investigated.

The possible uses of serpentine are reviewed in Part 4. Included are its possible use for producing compounds such as magnesium chloride and magnesia that can be used for the production of magnesium metal and magnesium compounds. Also discussed is the use of the silica residue from hydrochloric acid extraction for the production of silicate compounds and silica gel. Direct uses, or uses involving only heat treatment such as for refractories, adsorbent material, fertilizer, ion exchange material, and rock, are mentioned.

PART 1

SERPENTINE DEPOSITS

Virgil E. Barnes

INTRODUCTION

The serpentine deposits under consideration for this paper are of pre-Cambrian age and are situated in Gillespie, Blanco, and Llano counties of central Texas. Other serpentine deposits derived from rocks of Cretaceous age exist in the Balcones fault region of Texas, but these serpentines are notably low in magnesia; and since they are probably not applicable to any of the uses for serpentine discussed in this paper they will not be considered further. No

other deposits of serpentine are known in Texas.

The location of the more important deposits in central Texas is shown on the index map (fig. 1). The Coal Creek serpentine mass, by far the largest deposit (Pl. I), is astride the Gillespie-Blanco County line a short distance south of the juncture of these counties with Llano County. The most accessible deposits are in the Oxford area (fig. 3) just west of State highway No. 16 about 8 miles

south of Llano. Other small serpentine deposits are located in the Big Branch soapstone area (fig. 2), the Legion Creek area (fig. 4), and the Crabapple Creek area (figs. 5 and 6) of Gillespie County, and the Keener Branch area of Crabapple Creek (fig. 7) of Llano County.

Comstock (1891, p. 653), and by Simonds (1903, p. 73).

Paige (1911, pp. 10, 21, 90-93; 1912 (Folio), pp. 3, 4, 14; and 1912 (field ed. of Folio), pp. 25, 34, 100-101) is the first to give a lucid description of a central Texas serpentine deposit. According to

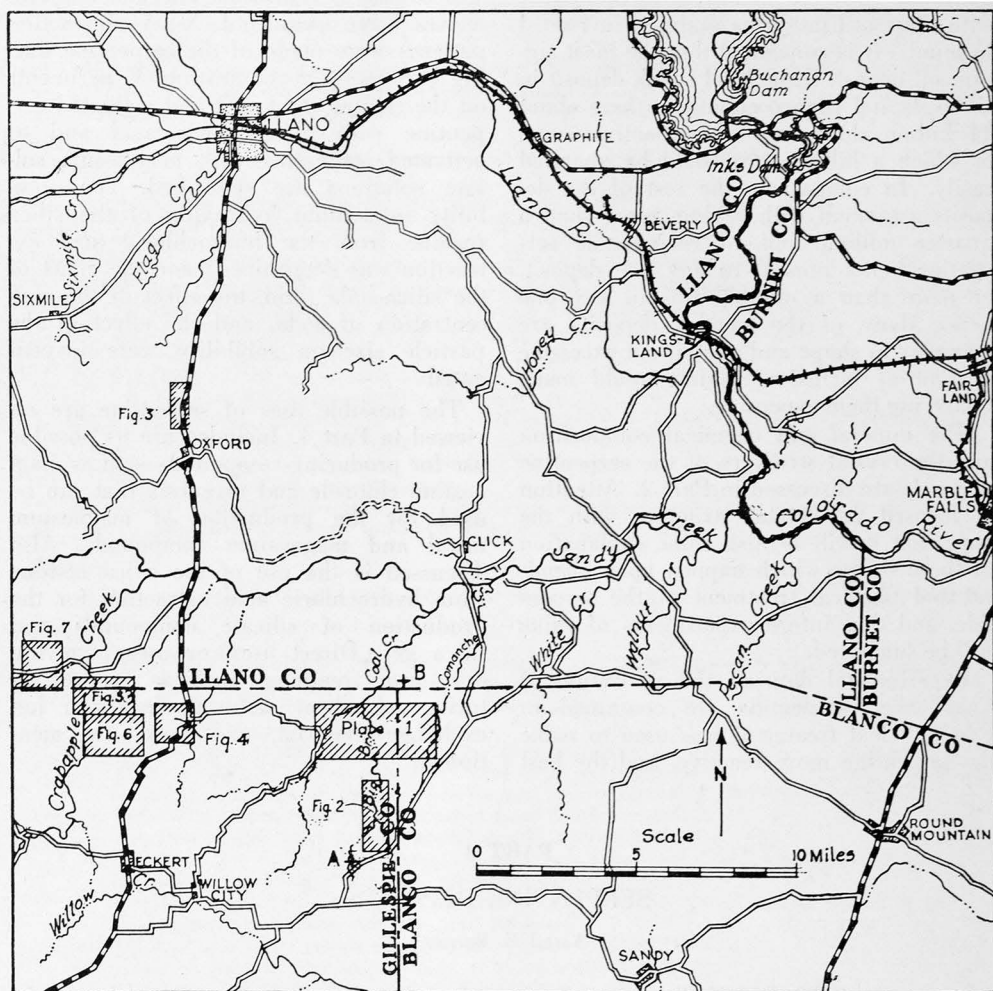


Fig. 1. Index map showing location of serpentine deposits in central Texas.

LITERATURE

The first mention of serpentine in central Texas, so far as known, is by Comstock (1890, p. 389) in which he lists localities at King Mountain, Llano County; near Long Mountain, Llano County; and in Gillespie County. This information is repeated by Dumble (1891, p. lxxiii), by

Schoch (1918, pp. 75, 188) a sample of serpentine from Gillespie County, sent to Dr. W. B. Phillips in May 1904, was analysed by O. H. Palm (Texas Min. Surv. Anal. No. 2831). The analysis is given in this paper under the discussion of the Coal Creek serpentine mass (p. 11). Udden, Baker, and Böse (1916, pp. 34, 157), apparently quoting Paige (1912), mention

serpentine on the Collins property in Llano County. If this is the same property which Paige described, it is south of Llano instead of west as stated by Udden, Baker and Böse, and is the serpentine in the vicinity of Oxford discussed in this paper. Sellards (1933, p. 33) mentions the presence of serpentine derived from intrusives mostly in the Packsaddle schist. Baker (1935, pp. 242-244) is the first to give a description of the serpentine mass in the vicinity of the Gillespie-Blanco-Llano County corner. Barnes (1940, 1943, 1945a), Barnes, Dawson, and Parkinson (1947, pp. 108-112), and Romberg and Barnes (1949) have contributed the bulk of the information about the serpentine deposits of central Texas. The following discussion is essentially a reorganization of that which already has been written, presented with the possible utilization of the serpentine in mind.

GEOLOGIC HISTORY OF THE LLANO REGION

A review of the geologic history of the Llano area will provide a background for a better understanding of the serpentine deposits. Paige (1910) summarized the geology of the Llano area and in 1912 reviewed for the first time the work which had been done in the area previous to 1912, defining some of the units as they are now recognized. The oldest rock unit recognized (Paige, 1912, pp. 3-4) is the Valley Spring gneiss derived by metamorphism from a thick series of sediments apparently of rather uniform composition. Paige states:

The Valley Spring gneiss is dominantly light colored and pinkish toned and comprises feldspathic and quartzitic schists, quartzites, wollastonite bands, granular acidic gneisses, and rare amphibolitic portions.

The light-colored portions are as a whole more or less schistose, are sugar-granular or aphanitic in texture, and are in many places distinguished with difficulty from rocks which may be granular granitic gneisses. The quartzites are light-colored, fine-grained, recrystallized equivalents of very quartzose sediments, and the amphibolites are not materially different from those in the overlying Packsaddle schist. The wollastonite bands are metamorphic equivalents of limestone and present the same structural relations.

The broadest and perhaps most marked distinction of the rocks of this formation from those of the overlying one is their more massive character.

The Packsaddle schist as recognized by Paige (1912, p. 4) is a metamorphosed series of sedimentary rocks that include

... mica, amphibole, and graphite schists and crystalline limestone. Some lighter-colored, more feldspathic bands, resembling quartzites, are included. There are also intrusives of diorite and gabbro, older than the granites and found locally in considerable amount. They have been separately mapped in only one locality, Elsewhere they have been included with the Packsaddle schist, though they are not a part of it.

As a whole the schists are characterized by an excellent cleavage, which in the main coincides with the original bedding of the sediments. . . .

Paige (1912, p. 4) recognizes at least one other gneiss in the Llano region about which he makes the following statement:

Gneisses formed almost certainly by the metamorphism of intrusive granites occur in the region. For example, a granitic crosscutting dike possesses much the same schistose nature as the beds which it cut. Red Mountain, a granite ridge in the southeast corner of the Llano quadrangle, is a noteworthy example of the same phenomenon. The granite of this ridge becomes progressively more gneissoid northwestward, until, at a point near Walker Peak, laminated structure is so evident that were the rock exposed only in this phase it could not be distinguished from beds that are believed to represent sedimentary strata.

Barnes (Romberg and Barnes, 1949, fig. 1) in mapping south and east from Red Mountain found the same to be true and designated these rocks as Red Mountain gneiss. A description of the rocks and a designation of the type locality should have been given in the text of the Romberg-Barnes paper but were inadvertently omitted. The Red Mountain gneiss is named for Red Mountain in the southeast corner of the Llano quadrangle, and the general character of the rock is described in the above quotation from Paige.

Another gneiss, the Big Branch gneiss, comprises much of the pre-Cambrian outcrop in the northwestern corner of Blanco County, the northeastern corner of Gillespie County, and some of Llano County, and is derived from an igneous rock of quartz diorite composition. Barnes (1945a, pp. 55-56) described the Big Branch gneiss as follows:

Foliation is well developed and lineation pitches steeply in a direction about S. 10° E. The Big Branch gneiss intruded the Packsaddle

schist and Valley Spring gneiss. Swarms of inclusions, mostly of Packsaddle schist, are arranged parallel to the foliation. The granites of the area and the pegmatites and aplites intruded the Big Branch gneiss.

Among the igneous rocks, Paige recognizes an earlier basic group. He states (1912, p. 4):

The rocks of this group were intruded earlier than the granites, but, though it is possible that those varieties of the granites which show evidence of pressure and metamorphism may be of nearly the same age, no relations were observed that might establish this point.

Paige mapped separately a few outcrops of the basic rocks mostly in the southeastern part of the Llano area and mapped the serpentine in the vicinity of Oxford. In the southeastern portion of the Llano quadrangle, Barnes (1945a, pp. 57-60) mapped many, mostly sill-like, intrusions ranging from diorite to hornblende and a few basic dikes that have not been classified.

Paige (1912, p. 5) mapped three types of granite—coarse grained, medium to fine grained including some coarse-grained varieties, and an opaline quartz porphyry (llanite). Stenzel (1935, p. 75) divides the granite into three main types:

1. Town Mountain granites; coarse-grained to porphyritic granites, commonly with large flesh-colored feldspars, typically exposed in the abandoned quarries on Town Mountain north of Llano.
2. Oatman granites; medium-grained, gray to pink, cataclastic granites, typically exposed in Oatman Creek southeast of Llano.
3. Sixmile granites; fine-grained, gray biotite granites, typically exposed in quarries near Sixmile.

The Town Mountain granite is the oldest, followed in order by the Oatman Creek granite (Stenzel, 1932, p. 144) and the Sixmile granite. The last igneous activity in the region was the intrusion of llanite dikes.

The pre-Cambrian was reduced to a surface having little relief except for hills of Valley Spring gneiss and aplogranite up to 800 feet high. The first sediments deposited on the pre-Cambrian rocks are of Middle or Upper Cambrian age. The Cambrian sequence from the base upward is sandstone grading upward into limestone followed by sandstone, limestone, shale, limestone, and dolomite. The Paleozoic geologic section exposed within a few miles of the serpentine mass is probably about 3,500 feet thick (Cloud and Barnes,

1948, pp. 258-260). Carboniferous rocks of unknown thickness were deposited above those listed; hence the maximum depth of burial of the serpentine by Paleozoic sediments is unknown.

Late in Paleozoic time the Llano area was shattered by normal faulting. There is no record of Permian, Jurassic, and Triassic sediments in the area, and by the start of Cretaceous time erosion had exhumed pre-Cambrian rocks in parts of the Llano uplift. Cretaceous sediments overlap the pre-Cambrian rocks at the surface, but only the Hensell sand member of the Shingle Hills formation (Barnes, 1948) is in contact with pre-Cambrian rocks. The base of the Cretaceous was probably not far above the present surface of the various serpentine deposits. Rocks of Fredericksburg age are probably the first to bury completely the Llano uplift. Other Cretaceous units of unknown thickness were deposited over the Llano region. Cretaceous rocks are now in contact with the pre-Cambrian rocks only along the south side of the region.

COAL CREEK SERPENTINE MASS, GILLESPIE AND BLANCO COUNTIES

Location.—The Coal Creek serpentine mass is on the southeastern side of the Llano uplift in Gillespie and Blanco counties (fig. 1). The nearest railroad is at Kingsland, 15 miles airline from the Comanche Creek end of the serpentine mass. A railroad route could be chosen down Comanche Creek and Sandy Creek cutting northward from the mouth of Cottonwood Creek past the eastern end of Packsaddle Mountain and thence across the Llano River to Kingsland, which would be about 16 miles long and of fairly even grade.

The nearest railroad terminal now accessible from the eastern end of the serpentine mass is Marble Falls, 24 miles distant by unimproved road. The western end of the serpentine mass is 25.5 miles from Llano, also a railroad terminus, by road, 20 miles of which is paved. This is the route over which the serpentine so far used has been trucked.

Geology.—The Coal Creek serpentine mass (Pl. I) is 3.7 miles long in an east-west direction and ranges from 0.3 to about 1.4 miles wide with important lobes at each end. The surface outcrop of the



Base from U. S. Department of Agriculture, Agricultural Adjustment Administration, aerial photographs flown by Kargl Aerial Surveys, Ltd., 1938.

serpentine is 2.54 square miles in area, of which 45 percent is in the attenuated 2.1-mile long central part of the mass, 20 percent in the western end of the mass, and 35 percent in the eastern end. The attitude of the main body of the serpentine, as determined from observations along its border and from observations of inclusions and alignments within the serpentine, suggests that it dips about 45 degrees to the south in its western part, steepening eastward to about 60 degrees where the mass curves northward. The attitude of the serpentine beyond this point was not determined. The outcrop shape and attitude of the serpentine suggest that it is essentially a thick sheet curved northward at each end, and such a sheet (composed of serpentine or its parent rock peridotite) should extend, as a minimum, at least several miles in depth.

The serpentine is bordered along the south and for the western half of its distance along the north by Big Branch gneiss. For the rest of the distance along its northern side, it is bordered by Packsaddle schist, which here is chiefly amphibole and mica schist containing numerous soapstone lenses. Additional pre-Cambrian rocks outcropping within 2½ miles of the serpentine mass are listed as follows: Valley Spring gneiss to the southwest; Red Mountain gneiss to the northeast; Town Mountain granite to the southwest and the southeast; and basic intrusives mostly to the north. The serpentine contains numerous inclusions of Packsaddle schist and a few originally thought-to-be altered Big Branch gneiss. These inclusions have not been mapped, but on aerial photographs each inclusion is marked by a dark area caused by a tree or group of trees growing on it. On north hill slopes and in valley bottoms not all trees, however, are on inclusions.

The serpentine is cut by aplite and pegmatite dikes which are entirely similar to ones derived from the Town Mountain granite. The serpentine is therefore definitely older than the Town Mountain granite. The evidence for the age relation of the Big Branch gneiss and the serpentine needs to be reviewed, especially as to the identification of inclusions in the serpentine originally thought to be Big Branch gneiss. If the serpentine is older than the

Big Branch gneiss, the conclusions reached in the paper by Romberg and Barnes (1949) will have to be modified. Additional collecting and analytical work would be necessary to settle this point, and since the age of the serpentine does not affect the conclusions in this paper, any additional work will be deferred until later.

The serpentine varies widely in color, texture, and structure. It ranges in color through a wide assortment of shades of green, from light yellowish green through dark green to very dark-colored rocks having a greenish cast. Samples are described by Barnes, Dawson, and Parkinson (1947, pp. 109–111) as follows:

B1-14—The sample of serpentine collected is only one type of several present in the area. It is light to medium dark green in color and has numerous light-colored, fibrous aggregates in it. These aggregates have a random orientation and are up to one-half inch in length. The serpentine does not polish well; a sawed surface, however, is attractive.

G-7—A deposit of serpentine is located about one-half mile south of the western end of the large serpentine mass The serpentine is composed of alternate bands of very dark green and very light green which have a marked contrast. The serpentine takes a rather dull polish.

G-8—The serpentine is a somewhat irregularly colored stone with colors ranging from a light greenish white to a deep greenish black. The light greenish-white serpentine has a semi-dendritic pattern with a background of olive-green. It is somewhat veined by narrow white veins which to some extent are stained limonitic brown. The limonitic brown color also penetrates the rock for a short distance along some of the veins. The serpentine takes a dull polish. Three terrazzo chip quarries are located in serpentine in this area. Much of the serpentine exposed in the quarries is slickensided and unsuited for producing dimension stone.

Locality G-7 is shown on Plate I as locality 86T-1-10C and G-8 as locality 86T-1-10B.

The specific gravity of the serpentine as determined from surface samples averages 2.48, which is higher than the value of 2.34 determined by the International Minerals and Chemical Company. The serpentine is relatively soft, being between about 3 and 4 of the Mohs scale of hardness. It is easily ground.

Composition.—The first analysis of serpentine (Schoch, 1918, p. 188) from central Texas was made by O. H. Palm as Texas Mineral Survey Analysis No. 2831.

The sample analyzed was sent to Dr. W. B. Phillips, May 1904, from Gillespie County. While the actual position from which this sample was obtained is not known, it is likely that the sample was from the Coal Creek serpentine mass. The analysis follows.

	Percent
SiO ₂	40.66
Al ₂ O ₃	1.70
Fe ₂ O ₃	5.20
FeO	3.06
MgO	35.50
CaO	trace
Na ₂ O	0.60
K ₂ O	0.25
H ₂ O	13.20
CO ₂	none
P ₂ O ₅	none
F	none
SO ₃	none
Total	100.17

The next analysis (Barnes, 1943) was made by R. B. Ellestad, of the Rock Analysis Laboratory, University of Minnesota, Minneapolis, of serpentine collected from a terrazzo chip quarry, locality 86T-1-9B, near Coal Creek, Gillespie County. The fluorine was determined by the Willard and Winter method. This analysis follows.

	Percent
SiO ₂	40.31
Al ₂ O ₃	0.43
Fe ₂ O ₃	6.71
FeO	0.70
MgO	37.63
CaO	0.05
Na ₂ O	0.01
K ₂ O	0.00
H ₂ O+	12.32
H ₂ O-	0.92
CO ₂	0.06
TiO ₂	0.01
P ₂ O ₅	0.01
Cr ₂ O ₃	0.41
MnO	0.04
BaO	0.00
NiO	0.30
F	0.01
S	0.03
	99.95
Less O	0.02
	99.93

Partial chemical analyses of five samples of serpentine were made by the International Minerals and Chemical Company in their Austin, Texas, plant. These analyses follow.

Sample No.*	MgO	SiO ₂	Fe as Fe ₂ O ₃	Cr ₂ O ₃	NiO
1	35.1	42.9	—	—	—
2	35.0	43.5	—	—	—
3	35.3	42.2	—	—	—
4	35.2	40.8	—	—	—
Average 1-4	35.2	42.3	—	—	—
5	36.7	39.7	7.3	0.47	0.34

*Locality of samples:

1. (16T-5-51E) Shaft, top 10 feet.
2. (16T-5-51E) Shaft, 60 feet down.
3. (16T-5-51E) Trench.
4. (86T-1-10D) Prospect pit near western end of serpentine mass.
5. (86T-1-9B) Terrazzo chip quarry.

In addition, spectrographic analysis of these samples shows iron to be a minor component; chromium and nickel range between about 0.1 and 0.3 percent; calcium and boron are present as traces of approximately 0.01 percent; and aluminum, copper, sodium, manganese, and zinc are present as faint traces of approximately 0.001 percent.

Chromite and magnetite in small segregations have been found in the serpentine, and zaratite, talc, and tremolite asbestos present in the serpentine seem mostly to be associated with inclusions. No minerals of value have been obtained from the serpentine, and so far the serpentine has been used only for terrazzo chips from quarries near the western end of the mass.

Chromite has been seen in five places in the eastern half of the serpentine mass. The westernmost locality, 86T-1-3A, about 2,000 feet east of Big Branch, has been test pitted and trenched, and a total of about one ton of chromite is piled about the pits. About three-quarters of a mile to the east of locality 86T-1-3A (at locality 16T-5-59E) about 200 pounds of chromite is scattered over the surface, and at locality 16T-5-59C, a mile eastward, about 1,000 pounds of chromite is scattered over the surface. A few stringers of magnetite were seen at locality 16T-5-59C, but no chromite was seen in place at any of the localities. A few schlieren-like streaks of chromite (locality 16T-5-51E) were prospected during 1942 and 1943, but nothing of importance was found. Another small mass of chromite in place at locality 16T-5-59C was found by R. W. Mathis near the south border of the serpentine mass in the small south-projecting lobe of serpentine in Blanco County. Test pitting failed to re-

veal more chromite than was seen at the surface.

The nickel mineral zaraitite (locality 16T-5-58H) is associated with an inclusion in the serpentine. Magnetite is abundant as small grains scattered throughout the serpentine, and small stringers of magnetite, such as those mentioned above (locality 16T-5-59C), are occasionally seen. A prospect hole (locality 86T-1-9A) along the northwestern margin of the serpentine exposes 21 inches of blocky magnetite in a schistose rock within a few feet of the serpentine boundary. A dip-needle examination shows that the magnetite extends for only a few feet on each side of the test pit.

Tremolite asbestos (locality 16T-5-51C) is exposed in a test pit near the eastern edge of the serpentine mass, and specimens of similar material were seen elsewhere about the mass. A short distance north of the test pit some chrysotile (locality 16T-5-51D) outcrops in veinlets a quarter to half an inch wide. The material while definitely of fibrous habit is not asbestos since it cannot be broken into fine enough fibers.

Soapstone is situated along the periphery of the serpentine mass in several places and occurs as inclusions within the serpentine either alone or associated with phases of the Packsaddle schist. A few inclusions of soapstone within the serpentine have been subjected to enough post-steatization movement to make them semi-translucent and superficially resemble better grade talc. The movement also has produced a schistosity which in turn is crumpled, rendering the talc unsuitable for use except for ground soapstone. Soapstone of this character has been seen only in small outcrops. The larger soapstone masses are beyond the borders of the serpentine, and at one locality, 86T-1-2A, actinolite crystals up to an inch in length have developed in the soapstone. Soapstone, while not being produced at present (1950) within the map area, is being produced a short distance to the south.

The percentage of included material within the serpentine mass has not been estimated, and without detailed mapping of the inclusions such an estimate is not reliable. However, the impression obtained from walking over the mass in

many directions is that less than 1 percent of included material is present, and that the greatest concentrations of inclusions are in two main areas. One of these is in the southeastern part of the serpentine mass, and the other is along the northern side of the mass extending west from Big Branch for about a mile.

The mineral composition of the serpentine in thin section appears to be relatively simple, with antigorite (possibly including some chrysotile) being predominant and the opaque minerals being present in subordinate amounts. A small amount of a fibrous material may be an altered remnant of one of the original minerals, probably an amphibole. The abundant network structure indicates that the rock was originally mostly olivine. Some of the opaque minerals are in well-shaped grains which indicates that they are primary, and some are distributed in irregular groups of dust-like particles suggesting that they are secondary, being formed during the serpentinization of the olivine. The opaque minerals are magnetite and chromite and, as mentioned later, are recovered on a magnetic separator from a finely ground sample.

The analysis of the serpentine from locality 86T-1-9B has been calculated by Barnes (1945a) into a theoretical mineral composition as follows:

	Percent
Serpentine (antigorite)	93.19
Magnetite	1.39
Chromite	0.67
Pyrite	0.06
Calcite	0.14
Opal	4.72

The molecular make-up of the "serpentine mineral" was arbitrarily chosen, placing all of the NiO in the nepouite molecule, since not enough sulfur is present to account for it as a sulfide, and all of the Al_2O_3 in the amesite molecule. All of the Cr_2O_3 was used for chromite, and all of the remaining FeO was used in magnetite. The remaining Fe_2O_3 was allotted to magnesio-cronstedtite, and the remaining MgO was allotted to antigorite. Since more than 80 percent of the "serpentine minerals" make-up is antigorite, following Winchell (1927, p. 375) it would be called antigorite. The theoretical molecular composition of the antigorite is as follows:

	Percent
Antigorite, $H_4Mg_3Si_2O_9$	85.3
Magnesiocronstedtite, $H_4Mg_2Fe_2SiO_9$	13.0
Amesite, $H_4Mg_2Al_2SiO_9$	1.2
Nepouite, $H_4Ni_2Si_2O_9$	0.5

Thin sections of the serpentine are described by Barnes, Dawson, and Parkinson (1947, pp. 110, 111) as follows:

G-7—Alternate laminae of light green and dark green serpentine comprise the rock. The dark green laminae are composed chiefly of network serpentine and a small amount of talc. One crystal within the dark green serpentine contains Schiller inclusions and resembles enstatite or clinoenstatite somewhat altered to bastite. Network serpentine has embayed the edge of the crystal and included some of the Schiller inclusions. Another area of similar Schiller inclusions has only a small amount of the original mineral present as laths having various orientations interleaved with talc, indicating that the mineral is altering to talc. Most of the Schiller inclusions are surrounded by talc and serpentine.

and a small amount of a fibrous mineral which may be a remnant of the original mineral. In addition to the primary magnetite grains, considerable finely divided secondary magnetite is concentrated in some of the serpentine.

Thermal analysis curves of the Coal Creek serpentine made by Shock show a small endothermal peak at 140° C., a large endothermal peak at 675° C., and a very sharp exothermal peak at 790° C. These data, as mentioned later (p. 31), indicate that the Coal Creek serpentine is an intimate mixture of antigorite and chrysotile.

An X-ray powder diffraction pattern of the Coal Creek serpentine (locality 86T-1-9B) made by Shock is compared in the following table with patterns listed by Selfridge (1936, p. 469) of deweylite, chrysotile, antigorite, and two other "serpentes."

Table 1. Interplanar spacing for deweylite, serpentine, chrysotile, and antigorite as listed by Selfridge (1936, p. 469) and for Coal Creek serpentine.

Line No.	Deweylite		Serpentine #44		Serpentine #1		Chrysotile		Antigorite		Coal Creek Serpentine	
	d Å	Est I	d Å	Est I	d Å	Est I	d Å	Est I	d Å	Est I	d Å	Est I
1	7.374	5	7.379	9	7.384	9	7.364	9	7.355	8½	7.35	10
2	4.594	8½	4.573	6	4.604	7	4.431	6	4.668	4	4.76	2.2
3	3.668	5	3.656	10	3.695	10	3.658	9½	3.641	9	4.55	3.6
4	2.457	8	2.477	9	2.463	8½	2.571	8	2.558	10	3.650	8.3
5	2.127	1	2.131	5	2.098	2½	2.424	8	2.186	7	3.545	2.7
6	1.717	5	1.721	2½	1.724	4	2.089	6	1.845	3	3.440	0.5
7	1.520	10	1.527	10	1.528	10	1.729	6	1.794	4	3.190	0.8
8	1.306	7	1.306	7	1.306	6	1.522	10	1.583	7½	2.955	0.8
9	1.040	¼	1.044	½	1.047	1	1.301	7	1.553	7½	2.880	0.8
10	.990	4	.990	4	.992	4	1.187	½	1.326	6	2.830	1.0
11	.878	3	.877	3	.882	3½	1.039	2	1.273	4	2.500	7.2
12	.761	1	.762	1	.762	1	.985	5	1.160	2	2.445	3.6
13	.728	1	.721	1	.727	1	.881	4	1.061	3½	2.145	1.6
14							.761	3	1.005	4	2.005	1.0
15							.727	1½	.979	3	1.792	0.7
16									.897	3½	1.536	4.3
17									.859	1	1.508	2.0
18									.831	2	1.502	2.0
19									.778	3	1.305	1.4
20									.743	3		
21												
22												
23												

The lighter colored areas are composed predominantly of talc, with some serpentine, and a small amount of chlorite. In both the light and dark-colored laminae, small elongated areas of opaque minerals are present in the same abundance, indicating that the rock may have been originally of uniform composition throughout.

G-8—The serpentine is composed predominantly of net-structured serpentine, magnetite,

The Coal Creek serpentine does not duplicate any of the other line spacings but does have a similar spacing. Some of the divergence may be due to the diffuse spectra of the serpentine minerals which makes it difficult to estimate closely the position of a line.

Origin.—Romberg and Barnes (1949) discuss the origin of the serpentine as follows:

Some generalizations on the time of formation of serpentine in relation to its emplacement are contained in geologic literature which do not seem to be supported by the Coal Creek serpentine mass. Hess (1939) suggests that water may be picked up by peridotite to form serpentine from water-bearing geosynclinal sediments. The Coal Creek mass did not intrude geosynclinal sediments, not at least at the level now being observed. If geosynclinal sediments existed above this level, which is doubtful, their contained water would not have been available for serpentinization of this deeper portion of the mass. As pointed out by Bowen (1947) it is unlikely that the water for serpentinization could be contained in the peridotite, and for the Coal Creek mass it looks equally impossible for sufficient water to have been picked up during the emplacement of the peridotite to form the serpentine.

The Town Mountain granite, as pointed out above, is probably later than the serpentine and could possibly have furnished the solution for serpentinization of the peridotite. However, the intervening rock shows little if any granitization and few aplites, pegmatites, and quartz veins come near to the serpentine. At least half of the serpentine is more than 2 miles from the nearest outcropping granite mass, and a regional gravity survey indicates that there is little probability of granite being as near beneath the serpentine. It, therefore, seems unlikely that serpentinization was influenced by the granite.

The production of serpentine within the zone of groundwater circulation has been little considered, except for serpentine of the type found along the Balcones fault zone (Lonsdale, 1927, pp. 139-141). If the Coal Creek mass is a result of ground water alteration, then there should be a limit to the depth to which the serpentine extends. The depth to which the serpentine extends cannot be observed directly, but an examination of the gravity field indicates that it is bottomed at a relatively shallow depth. When peridotite changes to serpentine, a large volume increase theoretically takes place, and in many deposits there is little evidence of the deformation that should accompany such a change. However, where serpentinization is a near-surface phenomenon, there is little confining pressure and the serpentine could expand upward with a minimum of shearing.

Chawner (1934) points out that folds in Eocene sediments above minutely faulted, fractured, and slickensided Upper Cretaceous serpentine indicates that the serpentine continued to expand after the sediments were deposited. The Cretaceous rocks were eroded exposing the ultrabasic rocks, indicating a period of time sufficient for the development of temperature equi-

librium before Eocene sedimentation. If serpentine continued to form during the deposition of Eocene sediments, then it seems likely that the serpentinization was caused by meteoric solutions.

Gravity observations.—A gravity survey (Romberg and Barnes, 1949) was made of the Coal Creek serpentine mass. A well-defined negative anomaly coincided with the serpentine mass, and from the shape of this anomaly and the knowledge of the surface geology some postulates about the mass are made. The serpentine extends to a depth of about 2,000 feet. The western end of the mass dips to the south, and the eastern end of the mass is about vertical. Peridotite probably exists beneath the serpentine.

A minimum estimate for the mass of serpentine present can be arrived at by measuring the area and multiplying by the estimated depth. This depth, of course, varies and may probably be taken to be 2,000 feet in the eastern part of the mass and 500 feet in the western. Dividing the area roughly into two parts and multiplying each by its estimated depth, yields a mass of 10^{10} metric tons (about 10.1^{10} short tons). If peridotite is present under the serpentine, the serpentine will be deeper at the east end, so the estimate of mass will be a minimum.

Reserves.—The serpentine is not within a contoured area; consequently the amount of serpentine above the level of the three main creeks cannot be closely estimated. However, 47 elevations of gravity stations having essentially random distribution (Pl. I) were obtained on the serpentine. The average elevation is 1,233 feet. Coal Creek, Big Branch, and Comanche Creek each have an elevation estimated to be near 1,100 feet where they leave the serpentine mass. This gives an estimated average thickness of 133 feet for the serpentine, or, using 5,000,000 tons for each foot of depth, about two-thirds of a billion tons of serpentine above drainage base. Allowing for mining losses caused by inclusions, wall irregularities, slope of walls, and including serpentine easily recovered beneath the drainage base, at least a billion tons of serpentine should be available.

SERPENTINE IN THE BIG BRANCH AREA, GILLESPIE COUNTY

Location.—The Big Branch area is in eastern Gillespie County south of the Coal Creek serpentine mass. The nearest railroad is at Marble Falls, a distance of about 27 miles by the most direct route. Soapstone from this area was being hauled by truck during 1948 to a grinding plant at Llano, a distance of about 38 miles.

Geology.—The Big Branch soapstone area, which also includes some serpentine, was mapped in detail by R. W. Mathis (Barnes, 1945a, fig. 13), and this map should be consulted by anyone wanting precise information. Figure 2 of the present paper is a generalization of Mathis' map showing the serpentine outcrops in the Big Branch area. The dominant rock is Big Branch gneiss which has invaded and assimilated much of the Packsaddle schist and possibly also Valley Spring gneiss. All that remains are numerous inclusions of Packsaddle schist, mostly amphibolite; masses of soapstone and tremolite; one outcrop of Valley Spring gneiss in the northwestern part of the map area; and a few small deposits of serpentine. The soapstone and serpentine are associated with Packsaddle schist, and if the one lone outcrop of Valley Spring gneiss is indicative, these deposits originally may have been near the Packsaddle schist—Valley Spring gneiss contact. The serpentine in part contains considerable tremolite and may not be suited for some of the uses mentioned later.

Composition.—Analyses were made late in 1949 of serpentine samples collected by Mathis (see Barnes, 1945a, fig. 13) from trenches dug mostly to give information about soapstone. The analyses were made primarily to settle the origin of the serpentine and associated rocks, and for this purpose it does not matter that the samples are from small masses. The analyses are given in Table 2; included are three serpentine samples: 55c, which has a composition, except for a high CaO content, very close to that of serpentines in the vicinity of the Valley Spring gneiss—Packsaddle schist contact; 63b, a sample containing considerable calcite; and 81, a sample high in SiO_2 and low in MgO. In addition three analyses were made of rocks associated with the serpentine: 63, soap-

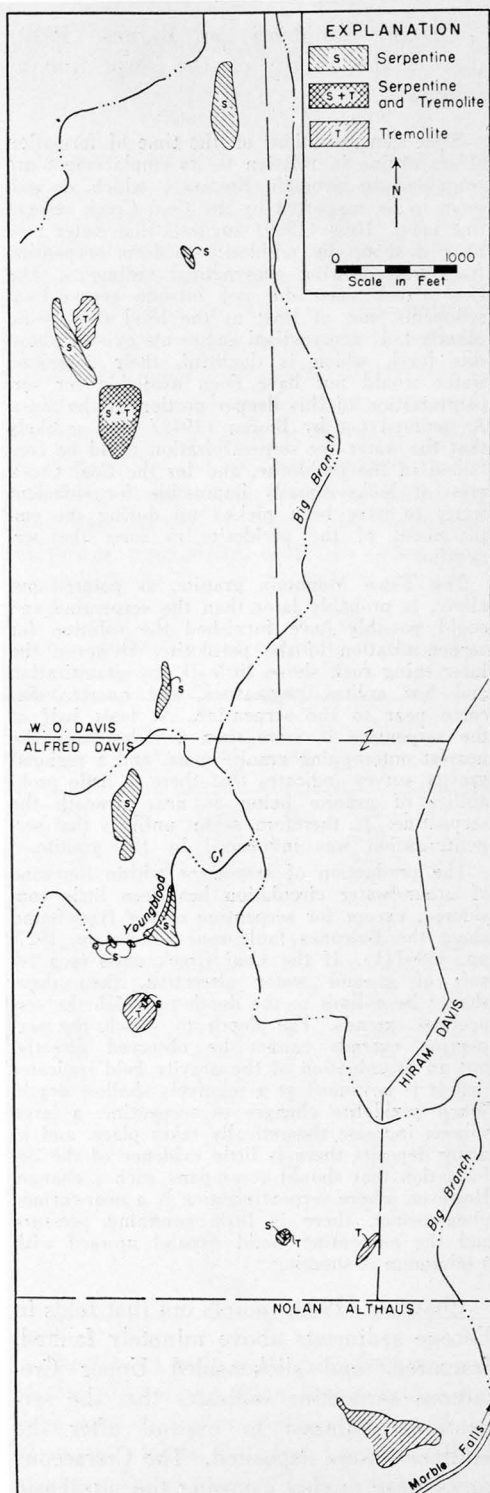


Fig. 2. Map showing location of serpentine outcrops in Big Branch soapstone area, Gillespie County, Texas.

stone; 55a, chlorite-vermiculite schist; and 63a, vermiculite schist. An analysis, B2, was made of a sample from one of the large tremolite masses.

All samples contain appreciable amounts of Cr_2O_3 and NiO , indicating a derivation from basic rocks of a peridotitic or pyroxenitic character. This negates the conclusion made earlier (Barnes, 1945a, pp. 73-74) that the tremolitic rocks were derived from calcareous rocks in the Packsaddle schist, and tends to throw doubt on the origin of the soapstones from calcareous rocks in the Packsaddle schist.

Reserves.—Five serpentine deposits in the Big Branch area are large enough to be quarried. The area of the deposits is about 440,000 square feet, which if a density of 2.5 is used, gives about 35,000 tons of serpentine per foot of depth.

MINOR SERPENTINE DEPOSITS IN SOUTHEASTERN PART OF LLANO UPLIFT

Youngblood Creek area.—A small serpentine deposit is located about half a mile west of the Fredericksburg-Marble Falls road in eastern Gillespie County (Barnes, 1945b, fig. 35). The deposit is only about 50 by 100 feet in size and consequently is of little value. A sample from this locality was described by Barnes, Dawson, and Parkinson (1947, p. 110) as follows:

The serpentine, in color, is a combination of light greenish white and very dark greenish

black arranged in a semi-dendritic manner. A small amount of intermediate green serpentine is mostly concentrated near veinlets in the serpentine. A dark brown limonitic material is also associated with the veinlets and to a small degree is scattered throughout the rock. A sawed surface of this rock developed a higher lustre than did one which was polished.

Near Llano-Blanco-Gillespie County corner.—A total of 13 serpentine deposits ranging from about 50 to 100 feet in diameter are arranged in an east-west 2,000-foot belt in Llano County about 400 to 800 feet north of the Blanco County line. The westernmost deposit is 600 feet northeast of the county corner. The serpentine is associated with soapstone, both of which are in Packsaddle schist. A geologic map of the area by Barnes (1945a, fig. 24) shows the location of the serpentine. These deposits are too small to be of much value especially since they are situated so near to the big Coal Creek serpentine mass.

SERPENTINE IN OXFORD AREA, LLANO COUNTY

Location.—The serpentine in the Oxford area is the most accessible in the Llano uplift. It is located about 8.5 miles south of Llano which is a railroad terminus and about 1.5 miles north of Oxford. The deposits are a fourth of a mile west of the paved Llano-Fredericksburg highway and are mostly high topographically. A quarry in the southernmost deposit, from which granules for road surfacing were produced, has been idle for a number of years.

Table 2. Analyses of serpentine and associated rock mostly from vicinity of Packsaddle schist—Valley Spring gneiss boundary.

Lab. No. ^a	Locality No. ^b	SiO_2	Al_2O_3 ^c	Fe_2O_3 ^d	CaO	MgO	Cr_2O_3	NiO	Ignition loss
478	86T-4-8D	40.28	1.08	8.34	0.67	34.77	0.56	0.18	14.06
479	86T-4-14E	40.61	4.04	7.12	0.06	32.11	0.42	0.28	13.34
480	86T-4-14F	39.32	2.98	8.27	1.25	33.77	0.46	0.22	13.29
481	86T-4-15C	36.60	2.67	11.98	0.06	33.69	0.95	0.53	13.43
482	149T-5-30I	39.39	0.84	7.69	0.25	37.38	0.44	0.28	14.52
483	149T-6-37F	40.11	2.12	8.34	0.38	34.78	0.88	0.29	12.51
628	55c	38.43	1.21	9.73	2.22	33.52	0.44	0.32	14.80
629	63b	35.73	1.21	9.94	9.49	25.81	0.41	0.31	17.81
630	81	49.62	1.38	9.81	0.37	27.92	0.44	0.51	10.40
631	55a	28.56	9.84	14.38	3.80	29.19	0.14	0.19	14.47
632	63	52.55	3.86	4.96	3.94	27.54	0.27	0.16	6.15
633	63a	48.51	5.01	17.42	2.68	17.15	0.18	0.14	8.94
634	B2	52.02	2.12	12.04	4.12	24.38	0.53	0.18	4.47

^aNos. 478-483 and 628-630 are serpentine; no. 631 is chlorite-vermiculite schist; no. 632 is soapstone; no. 633 is vermiculite schist; no. 634 is tremolite rock.

^bFor location of samples, see text figures as follows: 86T-4-8D, fig. 4; 86T-4-14E and 86T-4-14F, fig. 5; 86T-4-15C, fig. 6; 149T-5-30I, fig. 3; 149T-6-37F, fig. 7; 55c, 63b, 81, 55a, 63, 63a, B2, in Barnes (1945a, fig. 13).

^cThe remainder of R_2O_3 after deduction of Fe_2O_3 and Cr_2O_3 is reported as Al_2O_3 and includes P_2O_5 .

^dAll iron is reported as Fe_2O_3 even though part is present as FeO ; also includes TiO_2 .

Geology.—A geologic map of the area (fig. 3) shows that most of the serpentine is situated between two discontinuous bands of soapstone which are from 100 to 400 feet apart. The soapstone extends for about 1 mile and has serpentine associated with it mostly in its northern part. One outcrop of serpentine outside this belt has some vermiculite along its northern margin. The serpentine-soapstone belt is roughly parallel to the gradational Valley

Spring gneiss-Packsaddle schist contact but is mostly situated within the Valley Spring gneiss. A chemical analysis of the serpentine (locality 149T-5-30I) is included in Table 2.

Barnes, Dawson, and Parkinson (1947, p. 112) described the serpentine from the road material pit (L1-16) as follows:

The serpentine has a rather uniform medium green color and contains a few narrow disconnected white veinlets and many small black areas of magnetite. The serpentine takes a dull polish.

The serpentine (thin-section examination) is composed predominantly of serpentine and a rather large amount of magnetite. The serpentine varies considerably in structure and optical properties, suggesting that it has formed from more than one mineral. Several blades of serpentine up to 1 cm. in length have a higher and more variable birefringence than does most of the serpentine. This mineral appears to have been originally one of the amphiboles. Some areas of magnetite arranged in the manner of Schiller inclusions suggests that enstatite or hypersthene may have also been one of the original minerals. Much of the serpentine has a net structure which gives very little indication of the original mineral. Much of the magnetite of the serpentine is in grains, and the rest is in a form suggestive of Schiller structure. No secondary magnetite produced during serpentinization was seen.

Another sample (L1-46) from the larger serpentine mass on the high hill to the north is described (p. 112) as follows:

This sample of serpentine is the lightest colored of those examined. The color is grayish green but some areas apparently localized along joints are of much lighter color. Small black grains of magnetite are rather sparsely distributed throughout the rock. The serpentine takes a dull polish.

The serpentine (thin-section examination) is composed predominantly of serpentine minerals. A small amount of talc is present, most of which has a shredded appearance with serpentine developing around the edges and along the cleavages. The serpentine in many of these areas is stained by a limonitic appearing material. Magnetite is rather abundant mostly as original grains, some of which have been broken, with serpentine penetrating the cracks. Only a very small amount of secondary magnetite is present. The serpentine is of a network type and does not give much indication of the original mineral from which it was formed.

Reserves.—The serpentine deposits have been mapped on aerial photographs, scale 1 inch equals 660 feet. From these photographs the approximate areas of the five largest deposits were measured. The area of the deposits is about 235,000 square

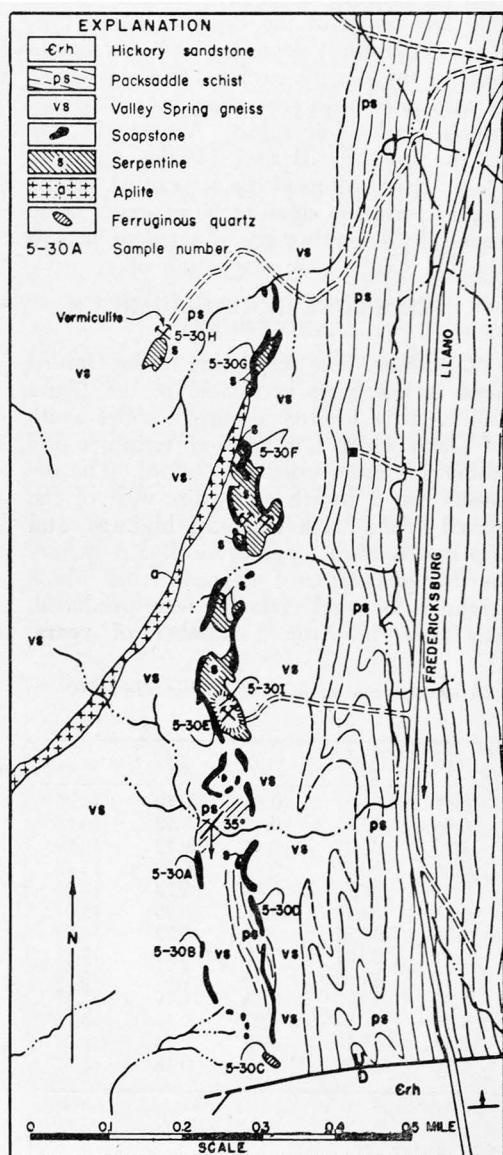


Fig. 3. Geologic map showing serpentine outcrops near Oxford, Llano County, Texas.

feet, which, using a density of 2.5, gives about 18,000 tons of serpentine per foot of depth.

SERPENTINE IN LEGION CREEK AND CRABAPPLE CREEK DRAINAGE BASINS

LEGION CREEK AREA, GILLESPIE COUNTY

Location.—The serpentine is located about 1 mile west of the paved Llano-Fredericksburg highway and about 1 mile south of the Llano County line. The deposit is 22 miles by road, 21 miles of which is paved, from Llano, which is the nearest railroad terminus.

Geology.—A map of the area (fig. 4) shows that the serpentine and soapstone form a belt of deposits which parallels the Packsaddle schist-Valley Spring gneiss

boundary and is within the Valley Spring gneiss. The serpentine and soapstone are not as closely associated as in the Oxford area, but otherwise the occurrence is very similar. The deposits are mostly on the western limb of a sharp syncline, the trough of which has been invaded by Big Branch gneiss. Town Mountain granite has irregularly intruded the rocks of the area, and the western edge of the Legion Creek granite mass is within three-fourths of a mile of the serpentine. Racket Mountain is a high hill of aplogranite belonging to the Oatman Creek granites, and aplites of uncertain affinity are present. A chemical analysis of the serpentine (locality 86T-4-8D) is included in Table 2.

Reserves.—The three deposits that are large enough to quarry have a surface area of about 180,000 square feet, which,

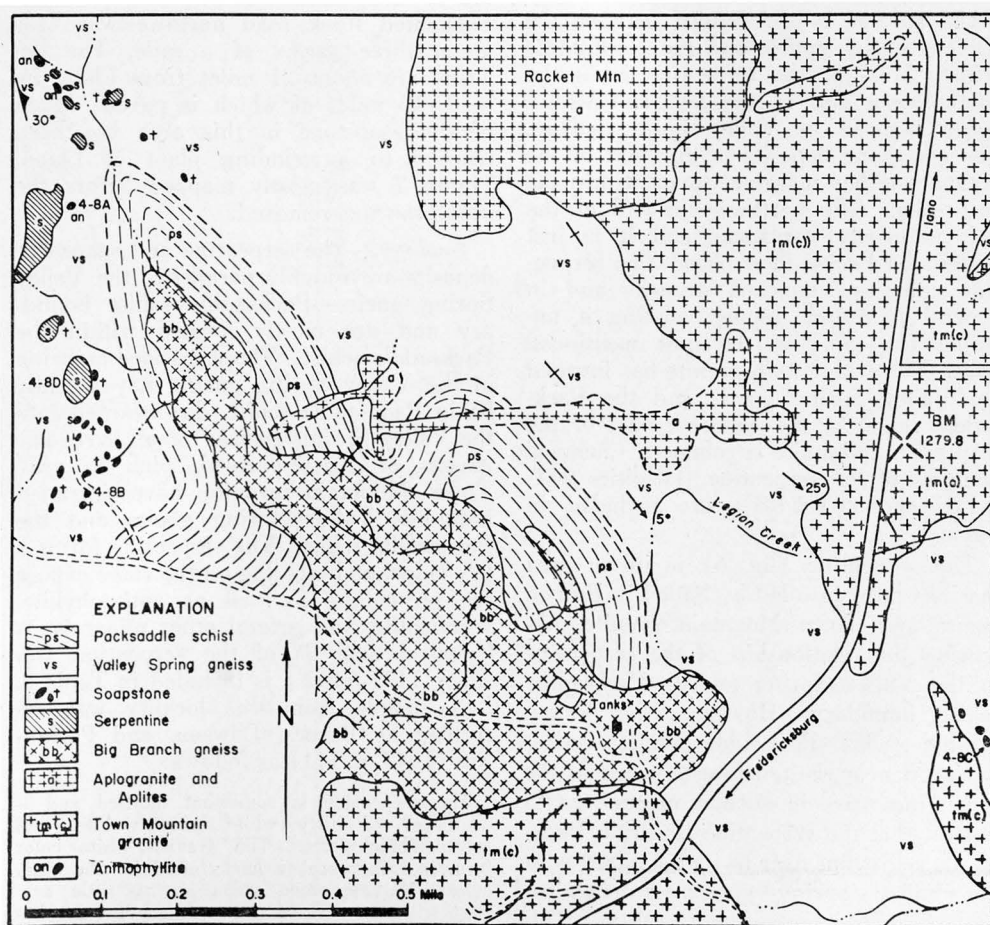


Fig. 4. Geologic map showing serpentine outcrops near Legion Creek, Gillespie County, Texas.

with a specific gravity of 2.5, gives about 14,000 tons of serpentine per foot of depth.

EAST SIDE OF CRABAPPLE CREEK,
GILLESPIE COUNTY

Location.—The serpentine (fig. 5) extends from the Llano County line on the west bank of Crabapple Creek southeastward intermittently for 1.7 miles. The distance from Llano, the nearest point on a railroad, is 21 miles by road, of which 16 miles is paved. Much of the soapstone associated with the serpentine has been trucked to a grinding plant in Llano. Figure 5 was mapped before the soapstone was removed. Another deposit of serpentine (fig. 6) is situated about 1 mile to the south in a rough, rather inaccessible area.

Geology.—The serpentine and soapstone (fig. 5) form a narrow belt of deposits parallel to the contact between the Valley Spring gneiss and the Packsaddle schist. Most of the serpentine is in the southeastern end of the belt and within rocks mapped as Valley Spring gneiss. The soapstone deposits in this part of the area are either marginal to or within the serpentine. The northwestern end of the belt is mostly soapstone, and it is just within the Packsaddle schist. The serpentine contains soapstone deposits and in general is rather impure, making it unsuited for some of the uses mentioned later. Town Mountain granite has invaded the Valley Spring gneiss and the Packsaddle schist in the southern part of the map area, and aplite is common. Chemical analyses of the serpentine (localities 86T-4-14E and 86T-4-14F) are included in Table 2.

The serpentine (fig. 6) is in an area that has been invaded by both Big Branch gneiss and Town Mountain granite, obscuring the relationship of the serpentine to the Valley Spring gneiss—Packsaddle schist boundary. However, the Valley Spring gneiss—Packsaddle schist contact is cut off near the northwestern end of the serpentine mass in such a manner as to suggest that the serpentine is within Packsaddle schist but near to its boundary with the Valley Spring gneiss. A chemical analysis of the serpentine (locality 86T-4-15C) is included in Table 2.

Reserves.—The deposits mapped in figure 5 are irregular in shape, contain soapstone deposits, and in general are rather impure. Upon revisiting the area after the soapstone had been quarried it appears that less serpentine is present than is shown on the map. At most, only a few hundred thousand tons of serpentine could be quarried.

The serpentine mapped in figure 6 is irregular in shape, contains inclusions, and has been intruded by aplite and pegmatite dikes. Its area is about 300,000 square feet, which gives about 23,000 tons of serpentine per foot of depth.

KEENER BRANCH AREA OF CRABAPPLE CREEK,
LLANO COUNTY

Location.—The Keener Branch serpentine deposits (fig. 7) are located a short distance northwest of those shown in figure 5. The deposits extend from near the Enchanted Rock road northwestward for about three-fourths of a mile. The deposits are about 21 miles from Llano by road, 16 miles of which is paved. Much of the soapstone in this area has been trucked to a grinding plant at Llano. Figure 7 was mostly mapped before the soapstone was removed.

Geology.—The serpentine and soapstone deposits are roughly parallel to the Valley Spring gneiss—Packsaddle schist boundary and are mostly located within the Packsaddle schist. Those mapped as being in the Valley Spring gneiss may actually be in Packsaddle schist, downwarped into the Valley Spring gneiss. Small, irregular masses of coarse-grained, pink to gray Town Mountain granite have intruded both the Valley Spring gneiss and the Packsaddle schist. The serpentine forms a low ridge, and pits dug on the ridge expose the serpentine, as well as anthophyllite, vermiculite, and several other minerals. A chemical analysis of the serpentine (locality 149T-6-37F) is included in Table 2.

A sample from this locality was described by Barnes, Dawson, and Parkinson (1947, p. 111) as follows:

The serpentine is somewhat mottled and is composed of dirty white, grayish-white, and greenish-black areas. The grayish white color forms a rather broken background for the other colors. Narrow green veins having little contrast with the rest of the rock are present but are not numerous. The serpentine takes a dull polish.

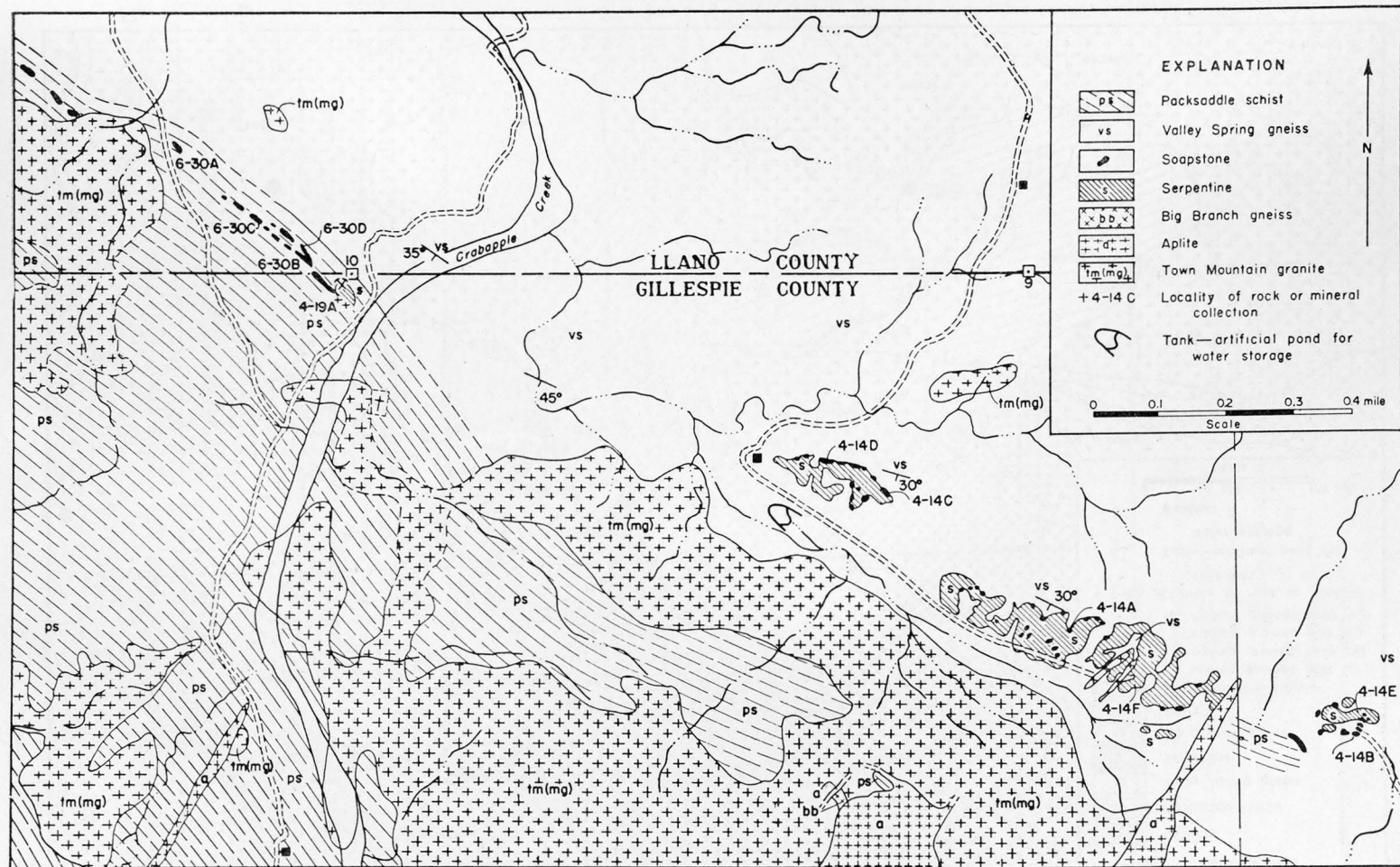
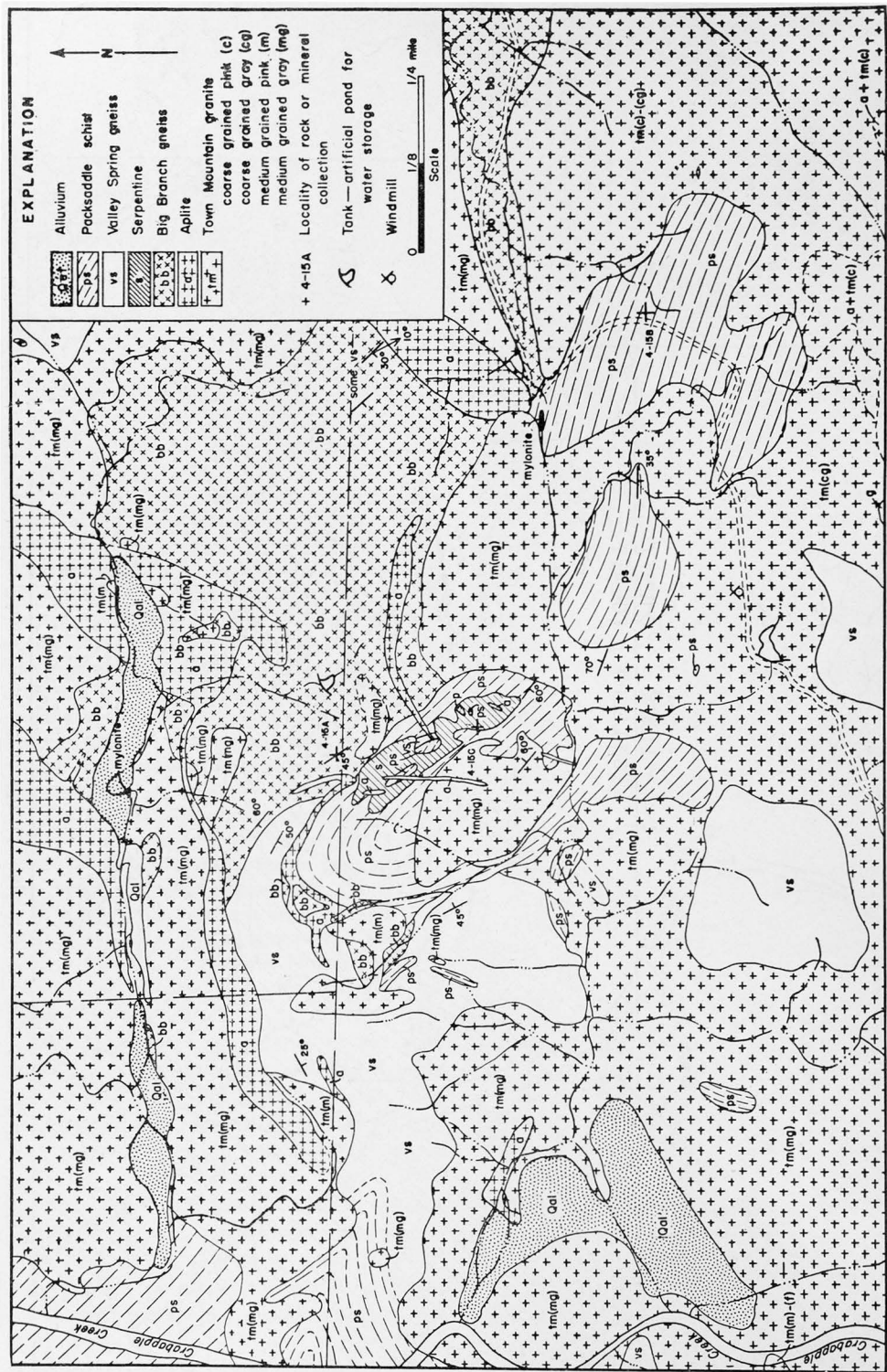


Fig. 5. Geologic map showing serpentine outcrops near Llano County line and Crabapple Creek, Gillespie County, Texas.



The serpentine (thin-section examination) is composed predominantly of net-structured serpentine, considerable talc, and a small amount of tremolite and magnetite. The magnetite is present both as primary grains and as finely divided secondary material mostly present at grain boundaries of the serpentine. Many of the serpentine grains are very light yellowish brown at the edges with a marked increase of color intensity at the centers. The serpentine grains are uniformly small and average about one-fourth of a millimeter in size.

Reserves.—The six small deposits mapped in figure 7 have an area of about 170,000 square feet, which, using a density of 2.5, gives about 13,000 tons of serpentine per foot of depth. However, the deposits are irregular in shape, contain many inclusions, and probably dip about 30 degrees to the south, which will limit the amount of serpentine that can be quarried.

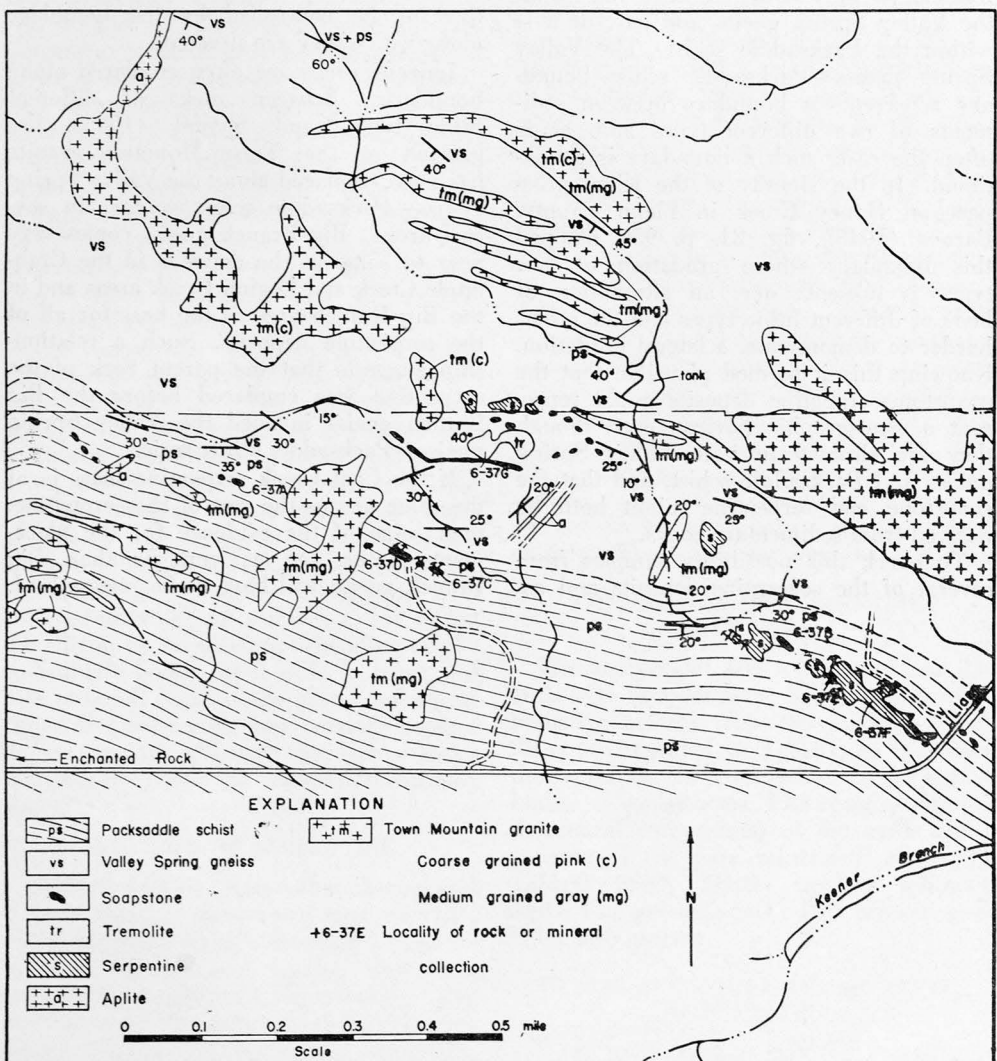


Fig. 7. Geologic map showing serpentine outcrops near Keener Branch of Crabapple Creek, Llano County, Texas.

ORIGIN OF SERPENTINE DEPOSITS IN
VICINITY OF PACKSADDLE SCHIST
—VALLEY SPRING GNEISS
BOUNDARY

It has been pointed out that the serpentine and associated soapstone in the Oxford area, in the Legion Creek and Crabapple Creek drainage basins, and possibly in the Big Branch area are parallel to the Valley Spring gneiss—Packsaddle schist boundary. Part of the serpentine is within the Valley Spring gneiss and part of it is within the Packsaddle schist. The Valley Spring gneiss—Packsaddle schist boundary represents a boundary between sediments of two different types and, as is often the case, such a boundary is gradational. In the vicinity of the Kiam prospect on Honey Creek in Llano County, Barnes (1945b, fig. 31, p. 95) mapped this boundary where gradation of two types is present; one, an alternation of beds of different lithic types and the other, harder to demonstrate, a lateral gradation. Knowing this it seemed plausible that the soapstone-serpentine deposits might represent a stratigraphic horizon even though they are situated in both Valley Spring gneiss and Packsaddle schist, and that the soapstone and serpentine might both be derived from sedimentary rocks.

To check this possibility samples from several of the serpentine deposits and as-

sociated rocks were analyzed by Mr. R. M. Wheeler, of the Bureau of Economic Geology, with special attention being given to the content of NiO and Cr_2O_3 . The analyses are given in Table 2. It is obvious that these rocks are higher in NiO and Cr_2O_3 than any rocks except the most basic ones, and that they could not be derived by the alteration of sediments. The emplacement of these rocks very close to the same horizon must either be fortuitous or be controlled by the boundary along which they are situated.

Igneous rocks are often emplaced along boundaries between rocks of different lithic types, and Stenzel (1935) has pointed out that Town Mountain granite has been emplaced along the Valley Spring gneiss—Packsaddle schist contact in several areas. Big Branch gneiss comes very near to some of the deposits in the Crabapple Creek and Legion Creek areas and in the Big Branch area is the host for all of the serpentine deposits. Such a relationship suggests that the parent rock of the serpentine was emplaced before the Big Branch gneiss invaded the Valley Spring gneiss—Packsaddle schist series.

If the Coal Creek serpentine mass is of the same age as the rest of the serpentine, then some of the evidence for the placement of its age as younger than Big Branch gneiss will have to be reexamined.

PART 2

MINERALS, COMPOSITION, AND STRUCTURE OF SERPENTINE

D. A. Shock

INTRODUCTION

The word "serpentine" is generally accepted as a rock name; it is also widely used as a mineral name. For the sake of clarity and in accordance with existing literature, serpentine is herein considered to be a rock containing the "serpentine" and associated minerals. Serpentine may be massive, compact, fibrous, lamellar, or columnar; most serpentines are brittle but some are fibrous and tough. The color is a variegated green with black, yellowish, and blue-green shades. Magnetite and chromite are usually present, and serpentine is often associated with talc, magnesite, and dolomite.

The serpentine minerals are hydrous magnesium silicates of the general formula $H_4Mg_3Si_2O_9$. Two principal minerals which are recognized are chrysotile, a fibrous asbestiform mineral, and antigorite, which may be a fibrous or a non-fibrous mineral. Replacement of magnesium by iron and nickel is common; calcium is found as a replacement less often. Aluminum is sometimes found, and it is believed that it can substitute for either the silicon or magnesium depending on the co-ordinate bonds, as it does in other silicate minerals such as the clays and micas. Other divalent metals may partially replace the magnesium, although they are of lesser importance than the metals mentioned above.

MINERALS OF SERPENTINE

Caillière (1936) states that X-ray and thermal analyses show antigorite, metaxite, picrolite, williamsite, dermatine, picros mine, bowenite, schweizerite, deweylite, chrysotile, baltimorite, marmolite, and cerolite to be identical. Nickeliferous garnierite, noumeite, pimplitite, nepouite, nickel-gymnite, roettisite, rewdanskite, genthite, and ferri ferrous forms of antigorite also have been described as separate minerals. She states that the antigorites can be divided into α and β groups according to their thermal analysis behavior. Efremov (1940) gives data contrary to this

separation, while Hargreaves and Taylor (1946) state that their work partially supports Caillière's data. The α form of antigorite is described as exhibiting an endothermic heat effect at 650° C. and a very sharp exothermic effect at 750° C. The first heat effect is accompanied by loss of H_2O , and the residue is amorphous. The exothermal heat effect is due to the rapid crystallization of enstatite and olivine. β -antigorite exhibits only the endothermal heat effect at 650° C.; the loss of H_2O and gradual crystallization of enstatite and olivine occur simultaneously. The preponderance of evidence (Selfridge, 1936; Gruner, 1937, 1939; and Efremov, 1940) is that α -antigorite and β -antigorite do not exist. Gruner (1939) also states that there is no indication of the formation of enstatite at temperatures between 560° C. and 650° C. In a letter of January 9, 1950, Dr. Gruner suggests that serpentine is frequently composed of an intimate mixture of antigorite and chrysotile. This may explain the results obtained by Caillière.

COMPOSITION OF SERPENTINE MINERALS

The analyses of 16 "serpentine" and 11 antigorite samples have been compiled by Selfridge (1936) from the literature, and these are repeated in Table 3 to illustrate the variation in composition and distribution of constituents. For comparison the theoretical composition of the oxide components of the pure mineral $H_4Mg_3Si_2O_9$ ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) are as follows: MgO , 43.5 percent; SiO_2 , 43.5 percent, and H_2O , 13.0 percent.

CRYSTAL STRUCTURE OF SERPENTINE MINERALS

X-ray studies show that the complexity and large number of silicate minerals are due largely to the ability of silicon to form complex atomic arrangements by the linking of the tetrahedral silicon-oxygen groups. These linking groups may be simple silicate structures, sheets or layers, straight chains, or three-dimensional link-

ages. The crystal structure of the serpentine minerals, while still not thoroughly defined, has been shown to be of the chain or layer type not unlike that of the amphiboles and some clays and micas.

Cronstedtite, chrysotile, and antigorite are of particular interest in that they bear the same formal relationship to the usual kaolin minerals as do the octophyllite to heptaphyllite micas. In other words, the positions having octahedral coordination are completely filled . . .

Table 3. Analyses of serpentine and antigorite; after Selfridge (1936).^a

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	H ₂ O	Na ₂ O	NiO	MnO	Total
SERPENTINE											
1	43.50	0.40	—	2.08	40.00	—	13.80	—	—	—	98.78
2	41.58	0.42	—	1.69	42.61	—	13.70	—	—	—	100.00
3	42.42	0.63	0.62	—	41.01	54	15.64	—	0.23	—	100.55
4	40.23	2.18	4.02	—	39.46	—	14.24	—	—	—	100.13
5	42.38	0.07	0.97	0.17	42.14	—	14.12	—	—	—	99.85
6	42.72	0.20	0.68	—	43.38	0.38	13.40	—	—	—	100.76
7	42.05	—	0.30	0.10	42.57	0.05	14.66	—	—	—	99.73
8	41.47	1.73	—	0.09	41.70	—	15.06	—	—	—	100.05
9	41.59	—	2.43	—	42.32	—	13.55	—	—	—	99.89
10	41.87	2.30	—	—	42.43	—	13.40	—	—	—	100.00
11	42.00	0.26	—	0.90	41.00	—	15.00	—	—	—	99.16
12	42.73	—	—	2.79	40.37	0.40	12.17	1.52	—	—	99.98
13	41.48	5.49	—	1.59	37.42	—	10.88	2.84	—	—	99.70
14	43.66	0.64	—	1.96	41.12	—	13.57	—	—	—	100.95
15	43.12	4.91	—	1.99	34.87	—	13.13	1.33	—	—	99.36
16	41.21	—	—	1.72	39.24	—	16.16	—	—	0.30	98.63
ANTIGORITE											
1	41.58	2.60	—	7.22	36.80	—	12.67	—	—	—	100.87
2	41.14	3.82	3.01	—	39.16	0.40	11.85	—	—	—	99.38
3	42.94	—	3.33	1.88	36.53	—	13.21	—	1.61	—	100.22
4	43.79	—	—	2.05	41.03	—	12.47	—	—	—	99.34
5	41.13	1.23	—	1.49	43.65	0.17	12.46	—	—	—	100.13
6	42.40	tr	—	1.56	42.50	tr	13.28	—	—	—	99.54
7	42.50	tr	—	0.95	43.15	tr	12.84	—	—	—	99.50
8	42.60	—	—	1.62	41.90	—	12.70	—	0.40	—	99.22
9	44.50	0.75	—	1.39	39.70	—	12.75	—	0.90	—	99.99
10	40.95	1.50	—	10.05	34.70	—	12.60	—	—	—	99.80
11	44.08	0.30	—	1.17	40.87	—	13.70	—	—	—	100.49

^aSample localities may be obtained from original article by Selfridge (1936).

One of the most recent discussions of the structure of the serpentine minerals and their relationship to the clay minerals is by Hendricks (1942, p. 276). In an abstract of his paper he states:

Minerals appearing in clays generally have layer lattice structures formed from (1) uncharged layers with hydroxyl ions on both surfaces; (2) hydroxyl ions on one surface and oxygen ions on the other; (3) oxygen ions on both surfaces; (4) charged layers with oxygen ions on both surfaces; or (5) two types of layers, one with hydroxyl ions on both surfaces, and the other with oxygen ions on both surfaces.

Serpentine is classed as group (2) along with kaolin minerals and cronstedtite. This relation is expanded upon by Hendricks (pp. 279-281) in his discussion on what is now known about the structure of the serpentine minerals and their relationship to the other silicate minerals as follows:

A structure for chrysotile asbestos was advanced by Bragg and B. E. Warren [Warren and Bragg, 1930] which satisfactorily explained its fibrous character. However, many of us, including Warren, knew that some of the X-ray diffraction data were not satisfactorily explained by this structure, particularly the peculiar diffuseness of reflections from planes with the *k* index other than zero. Warren and K. W. Herring [1941] now apparently have found the correct structure, which is simply that of kaolinite with 3 Mg ions substituted for 2 Al ions. Pauling [1930] had pointed out that such a substitution would be expected so to distort the lattice, owing to the greater size of the Mg⁺⁺ ion, as to render it unstable. Actually, this strain seems rather to restrict the width of a layer to a few units of structure say 30-100Å as shown by electron microscope photographs [Muller and Ruska, 1941]. Growth along the plate, however, is still permitted; in other words, the strain is taken up in one direction. Chrysotile is thus considered to be an aggregate of kaolin-like plates perhaps only one or a few layers thick. The fibrous character is due to the extreme extension of the plates in

one direction. Other clay minerals probably also will be found to develop as fibers under some conditions.

A possible structure has not yet been advanced for antigorite, and caution should be exercised in discussing it. Gruner [1937] has shown that chrysotile and antigorite have powder-diffraction patterns that do not appear to be similar. Inspection of his data, however, indicates that the underlying layer structures are possibly the same and that antigorite might differ from chrysotile only in the type of lattice limitation. The $Mg_3Si_2O_5(OH)$ kaolin-type layers of antigorite might be more nearly equidimensional and somewhat broader than those of chrysotile. In other words, the strain caused by the presence of Mg^{++} ions would be isotropically distributed in a layer—a condition that could arise from a different rate of formation. Limitation of length would be more likely to permit several layers to be superimposed as in the kaolin minerals. We thus have the following series: (1) Nacrite, lattice not limited; (2) Chrysotile, lattice limited in 2 dimensions, width of layers and their number; (3) Antigorite, lattice limited in 2 dimensions, width and length of layers. Optical properties are determined by the lattice limitations, and thus antigorite and chrysotile could readily have different optic signs.

Warren and Bragg (1930, p. 201) in discussing antigorite state:

The unit cell is monoclinic, with $a = 14.66\text{\AA}$, $b = 18.5\text{\AA}$, $c = 5.33\text{\AA}$ and $\beta = 93^\circ 46'$ The structure indicates a formula expressed by doubling the usual molecule $H_4Mg_3Si_2O_5$ and writing it $(OH)_4Mg_6Si_4O_{11}.H_2O$. There are four of these molecules in the unit cell.

. . . Each silicon is surrounded by four oxygens tetrahedrally arranged. Part of the oxygens are shared between neighbouring tetrahedra, forming endless chains of silicon-oxygen tetrahedra lying parallel to the "c" axis. The chains have a composition Si_4O_{11} , and are similar to the chains previously found in the amphiboles. Between the sets of chains are sections of Mg and OH arranged as in Brucite.

This structure as depicted by Warren and Bragg consists of a chain of 4 silicon-oxygen tetrahedra, 5 Mg^{++} ions holding 6 OH^- ions with one Mg^{++} bonded between the layers, and one H_2O held between the 4 silicon-oxygen tetrahedra. Hendricks, as noted above, believes that the structure of antigorite is similar.

A knowledge of the exact structure of the serpentine minerals is helpful in projecting ways that their structure might be altered to advantage. Chemical and physical means can be used to produce desired alterations in the structure of the serpentine minerals, and a possibility of other desired changes being feasible should not be overlooked. Thus if the structural requirements were definitely known, it may be possible to produce chrysotile asbestos from antigorite, or the serpentine minerals might be made to behave as the catalytic clays. It is with these points in mind that the structure and physical properties of the minerals have been stressed.

PART 3

EXPERIMENTAL DATA ON SERPENTINE

D. A. Shock and W. A. Cunningham

HEAT TREATMENT OF SERPENTINE

ACTIVATION—DECOMPOSITION WITH HEAT

The decomposition of serpentine has been demonstrated by the work of Rudneva (1939), Kurnakov and Chernukh (1926), Hargreaves and Taylor (1946), and Caillère (1936). As the serpentine is heated it loses water and its crystalline structure becomes so disrupted that an X-ray diffraction pattern cannot be obtained. With continued heating at any given temperature, or with increase in temperature, rearrangement takes place and new materials form. Brandenburg (1940) discusses the possibility of making the magnesium more available through control of heat treatment. He points out that within certain prescribed temperature limits, the extraction of magnesium is a function of the temperature to which the serpentine has been treated prior to the extraction but that when heated at temperatures below or above those activating temperatures the serpentine is relatively inactive. When similar studies were made of the Coal Creek serpentines they were found to exhibit general characteristics similar to those described by Brandenburg (1940), but, in addition, rather important data were obtained which appear to be applicable to other serpentine rocks.

DECOMPOSITION CURVES

The term "activation" is used herein for heat treatment known to render the serpentine more active chemically. Most of the heat treatment was carried out on relatively finely ground Coal Creek serpentine from Gillespie County. The rock was reduced to desired size by crushing to approximately one-quarter inch in a jaw crusher and then by passing it twice through a disk pulverizer, after which all material passed a 100-mesh screen and 75 percent passed a 200-mesh screen. A thermostatically controlled laboratory muffle, in which the temperature could be maintained within 5° C. of that desired, was used for activating the serpentine. The weighed samples, depending upon the

amount, were placed in either porcelain crucibles or flat dishes so that loss in weight could be determined at various time intervals.

Weight loss plotted against time for various temperature levels (fig. 8) shows that there is a considerable difference in both the rate of decomposition and the composition of final product between 500° C. and 600° C. At 600° C. the decomposition approaches a limiting value in four hours; at higher temperatures the limiting value is approached much more rapidly. At temperatures of 500° C. and below, the limiting value is approached very slowly and for practical purposes may never be reached. Experience shows that 48 hours is insufficient to give 14 percent loss at 500° C.

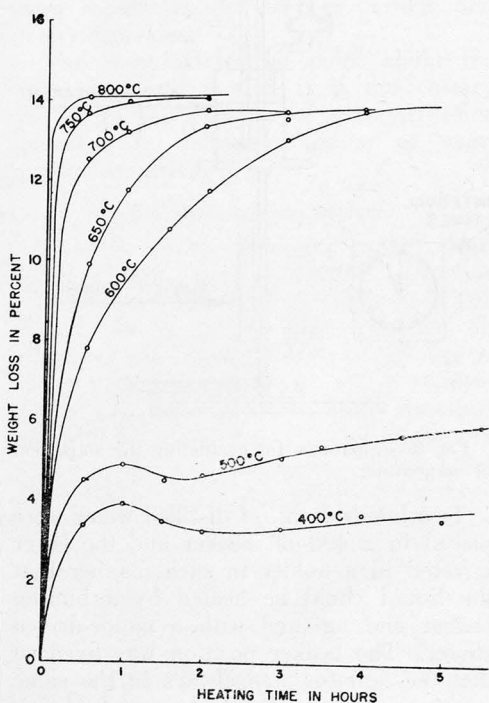


Fig. 8. Loss in weight versus time of calcination at various temperatures for Coal Creek serpentine.

MEASUREMENT OF ACTIVITY

Brandenburg (1940) measured the activity, or available base, by determining the amount of benzoic acid with which a given weight of activated serpentine would react in a standard time. A test which gave comparable results was used in this work for evaluation of activation which, while similar in nature to that of Brandenburg, gave results in much shorter time. The evaluation was made in an apparatus shown in figure 9 according to the following procedure:

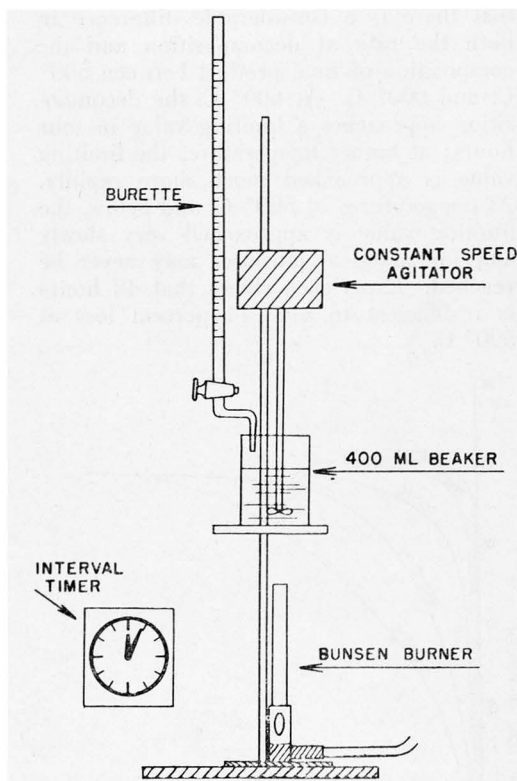


Fig. 9. Apparatus for evaluating the activation of serpentine.

Two hundred ml. of distilled water were placed in a 400-ml. beaker and the latter inserted in a holder in such manner that the liquid could be heated by a bunsen burner and agitated with a motor-driven stirrer. The beaker position was fixed so that the agitator was always in the same position in the beaker. The speed of agitation was kept constant by a voltage regulator. Ten ml. of 1.0 normal hydrochloric acid were added to the beaker along with

two drops of methyl orange indicator. The solution was then heated to boiling while being vigorously agitated.

A 2.000-gram sample of the serpentine was added to the boiling solution, and the length of time required to turn the red of methyl orange to a definite yellow was noted. The values thus obtained are reproducible to within ± 5 percent of the total time, which, in the more active ranges, is less than one minute; neutralization times of more than five minutes were not so consistently reproducible. The activity of the sample was taken as the reciprocal of the neutralization time in minutes. The most reactive samples required 0.25 minute to neutralize or had an activity number of 4. By this method the relatively unreactive samples requiring more than one minute to neutralize would have activity numbers less than 1.

REACTIVITY OF HEAT-TREATED SERPENTINE

The activities of the samples which furnished the data for figure 8 were determined in the manner just described. The results of plotting the activity number against the heating time on logarithmic coordinate paper at various temperature levels are shown in figure 10.

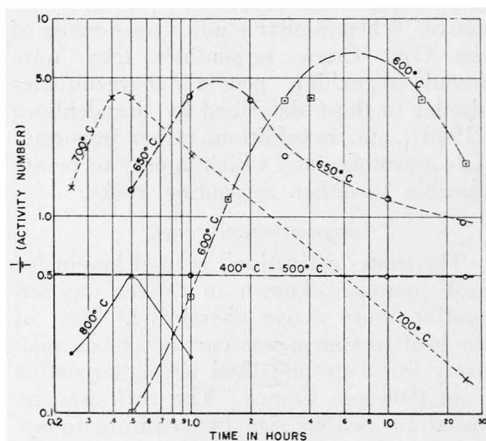


Fig. 10. Degree of activation of Coal Creek serpentine at various temperature levels.

It is evident that the activity of the serpentine is a function of both time and temperature, that is, the same degree of activation can be obtained by heating at a lower temperature for a longer period of time which can be obtained in a shorter period of time at higher temperature. It

is also evident that there are limits on both temperature and time of activation. Figure 11 is a graphical representation of the active area, compiled on the basis of the data in figures 8 and 10. The shaded area represents activated serpentine with under-activated material on the lower temperature side and dead burned material on the higher temperature side. The activated area practically disappears above $750^{\circ}\text{C}.$; yet it is possible that higher temperatures and very short time intervals may accomplish activation along with disruption of the crystal structure. If so, a superior activated product might be obtained by using a treatment similar to that used in flash expanding vermiculite where the problem is of a similar nature. Laboratory equipment suitable for conducting such trials was not available.

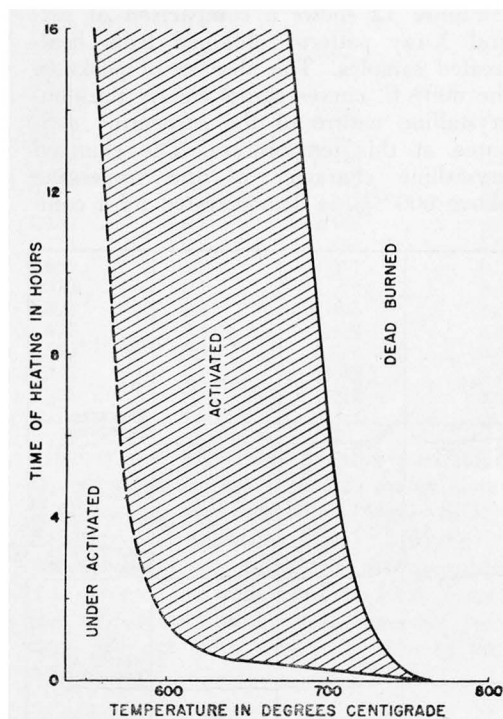


Fig. 11. Optimum time and temperature ranges for activation of Coal Creek serpentine.

EFFECT OF PARTICLE SIZE

The experiment just described gives activation data for relatively finely ground material, 75 percent of which passes a 200-mesh screen. In order to determine the effect of particle size on activation, samples of different screen size were activated

at the same temperature for the same time and their reactivity determined.

Raw serpentine was ground, screened into six sizes, heated at $700^{\circ}\text{C}.$ for three hours, and the activity number determined. The data thus obtained are presented in Table 4; in columns 5 and 6 are shown the arithmetic average sieve openings and the estimated surface areas of a 2-gram sample of the indicated size. The calculated surface areas shown are for comparison purposes only and cannot be considered as absolute. The calculations were based on the following assumptions: (1) an apparent specific gravity of 1.4; (2) cubical particles whose side dimension is the arithmetic average of the openings of the sieves through which the particular sample passed and on which it was retained.

Though qualitative only, the data indicate that maximum activity numbers can be obtained with particles no finer than 100 mesh (0.149 mm.). This, of course, was anticipated since reactions between solids and liquids are functions of the solids surface area and the latter increases very rapidly as the average particle diameter decreases.

The most interesting point about the foregoing data is that it is unnecessary to go to the expense of extremely fine grinding to obtain maximum or near-maximum activity.

X-RAY DIFFRACTION STUDIES

Caillière (1936), Rudneva (1939), Hargreaves and Taylor (1946), Efremov (1940) and Haraldsen (1928) have followed the course of heat treatment of serpentine by X-ray diffraction studies in order to determine the resulting changes that take place in the crystal structure. From their work it is evident that the serpentine minerals decompose, losing water on heating, with a subsequent loss of crystalline structure. With increasing temperatures, a rearrangement takes place, and X-ray patterns show the presence of new crystalline materials. In general it is noted that the characteristic crystalline structure of serpentine disappears almost entirely between $500^{\circ}\text{C}.$ to $600^{\circ}\text{C}.$ Olivine is formed after decomposition at temperatures above $600^{\circ}\text{C}.$; at higher temperatures, above $1,000^{\circ}\text{C}.$, other minerals have been noted, such as periclase (MgO),

Table 4. Effect of particle size on activity of Coal Creek serpentine.

National Bureau of Standards sieve number		Sieve opening Millimeters		Arithmetic Average	Estimated surface area of 2-gram sample Square centimeters	Activity number 1/T
Through	On	Through	On			
8	16	2.38	1.19	1.735	50	0.92
16	25	1.19	0.71	0.95	90	1.13
25	40	0.71	0.42	0.565	155	1.39
40	80	0.42	0.177	0.298	288	1.58
100	200	0.149	0.074	0.112	760	2.00
200	—	0.074	—	0.05*	1,710	2.00

*Assumed.

enstatite (MgSiO_3), and amorphous silica (SiO_2). The literature is not in good agreement on the temperatures at which the transformations take place; this may be due in part to the variation in mineral constituents in the different samples. It is evident, however, that the crystalline form is disrupted by heat treatment, and recrystallization takes place when the serpentine is heated to some higher temperature.

X-ray examination of Coal Creek serpentine which has been subjected to heat

treatment checks the general behavior noted in the literature, showing gradual disappearances and dispersion of the lines in the X-ray diagrams, with the appearance of olivine at higher temperatures.

Figure 12 shows a comparison of several X-ray patterns obtained from heat-treated samples. The absence of peaks in the 600°C . curves shows clearly the non-crystalline nature of the serpentine activated at this temperature. The changed crystalline character of the serpentine above 600°C . is demonstrated by a com-



Fig. 12. X-ray diagrams of Coal Creek serpentine, both raw and heat treated.

parison of the curves for untreated serpentine and for serpentine heated to 400° C., with curves for serpentine heated to 800° C. and 1,000° C. That the end product at 1,000° C. contains mostly olivine or enstatite is indicated by a comparison of the crystal plane spacings found in the heated sample with those of natural olivine, as shown in Table 5.

Table 5. Comparison of crystal planes of olivine and heat-treated Coal Creek serpentine.

Heat-treated Coal Creek serpentine 1,000° C. - 3 hours		Olivine Data from ASTM Tables	
d_{hkl} \AA	I/I_1	d_{hkl} \AA	I/I_1
5.03	0.1	5.10	0.6
3.87	0.5	3.95	0.4
3.71	0.2	3.79	0.2
3.465	0.2	3.53	0.3
3.275	0.2	—	—
3.156	0.4	3.02	0.7
2.985	0.3	—	—
2.880	0.5	—	—
2.755	0.7	2.792	0.7
2.690	0.2	—	—
2.510	1.0	2.516	0.7
2.455	0.9	2.466	0.8
—	—	2.261	0.8
2.150	0.2	2.162	0.5
1.174	0.7	1.744	1.0
1.666	0.2	1.667	0.3
1.570	0.1	1.569	0.3
1.492	0.3	1.495	0.6
1.477	0.4	1.478	0.8
1.390	0.2	1.393	0.8
1.345	0.2	1.343	0.7
1.310	0.1	1.314	0.6

Lines not explained by this particular olivine structure are shown to match some of those in the enstatite ($\text{MgO} \cdot \text{SiO}_2$) structure and nephrite ($2\text{CaO} \cdot 5(\text{MgFe}) \cdot 8\text{SiO}_2 \cdot \text{H}_2\text{O}$) structure. It is also possible that some of the weak lines are from hematite (Fe_2O_3). The crystal structure patterns did not show any indication of the formation of crystalline MgO or SiO_2 .

THERMAL ANALYSES OF COAL CREEK SERPENTINE

The thermal analysis curves of the Coal Creek serpentine are similar to those obtained by Caillière (1936) from material which she identified as α -antigorite. The curves probably indicate instead that both antigorite and chrysotile are present. Curves for both raw and activated serpentine are shown in figure 13. Raw serpentine exhibits a large endothermal peak at

675° C. and a sharp exothermal peak at 790° C. The activated serpentine, having lost its water of crystallization, does not give the large endothermal peak; the sharp exothermal peak, however, remains. The small endothermal peak at about 200° C. is not explained; it is also present on some of the curves obtained by Caillière.

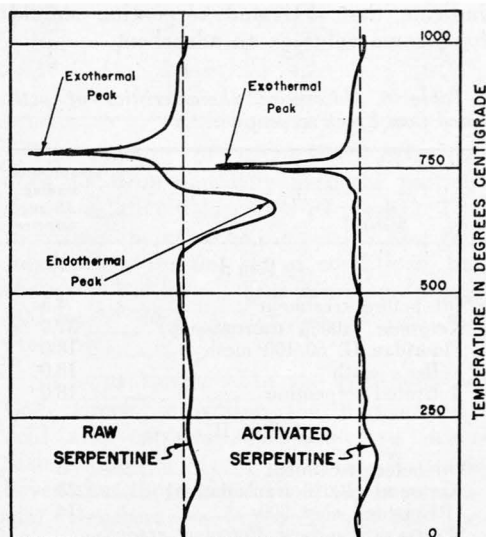


Fig. 13. Thermal analysis curves for raw and activated Coal Creek serpentine.

ADSORPTION PROPERTIES OF ACTIVATED COAL CREEK SERPENTINE¹

Activated serpentine was compared with a number of commercial adsorbents used to decolorize oil and was found to have some value as an adsorbent. Ten-cc. samples of crankcase oil were thoroughly shaken with the adsorbent and allowed to settle. The comparison was made by measuring the amount of light transmitted through the liquid by a tungsten lamp, using the amount of light transmitted through water-white kerosene as a standard. The transmitted light is allowed to fall on a photocell, and the readings are recorded in micro-amperes. Comparative data for the various materials tested are recorded in Table 6.

Runs I and II were made on different instruments so that the values for the oil and kerosene were not the same. Both runs show by this method of testing that

¹Investigations now in progress, using additional samples of Coal Creek serpentine, have not confirmed the data obtained earlier and reported in this section. Further studies will be made. W. A. Cunningham, June 1950.

the activated serpentine retains about the same amount of color bodies as the commercial clays. Acidic compounds should be removed better by activated serpentine than by most clays because of the basic nature of the reactive magnesium oxide. However, no data have been gathered to support this. The tests which were run indicate that activated serpentine should have some value as an adsorbent.

Table 6. Adsorptive characteristics of activated Coal Creek serpentine.

Material	Transmission reading Micro- amperes
Run I	
Oil before treatment	4.5
Kerosene (100% transmission)	37.0
Fluoridan G, 60/100 mesh	18.0
Fuller's earth	18.0
Activated serpentine	18.0
Run II	
Oil before treatment	3
Kerosene (100% transmission)	23
"Riverside" clay 200	14
Westvaco adsorbent, Percolent grade 30-60	14
Fuller's earth, Bennett & Clark, 200-mesh	13
Fuller's earth, sample from stock room of The University of Texas, Department of Chemistry	15
Activated serpentine (3 hours at 650° C.)	13

The adsorbent characteristic of serpentine developed during heat treatment is probably caused by (1) disruption of the crystal structure through removal of water, thus causing a tremendous increase in surface area; and (2) production of unsatisfied bonds where the water was removed.

CHEMICAL TREATMENT OF SERPENTINE

SOLUBILITY OF RAW SERPENTINE

The raw serpentine minerals, contrary to most silicate minerals, are readily amenable to chemical treatment. The serpentine minerals are attacked by the mineral acids as shown by Terpugov and Portugalova (1938) and B. A. Peacock (1919). Mellor (1925) reports that they are attacked slightly by even such weak acids as carbonic. Two patents have been issued

covering the treatment of serpentine with caustic soda (sodium hydroxide). Samuel Peacock (1917b, U.S. Pat. 1,250,216) claims that the silica is dissolved in the caustic soda, leaving the magnesium oxide, and Jackson (1918, U.S. Pat. 1,254,230) claims that an acid-soluble magnesium silicate is formed. Decomposition of serpentine minerals by chlorine gas at high temperatures, by concentrated solutions of ammonium chloride, and by concentrated solutions of calcium chloride and of ferrous sulfate have been reported by V. F. Belik (1939), M. A. Oganessian (1938), and S. Peacock (1917a). The latter's work is covered by U.S. Patent 1,250,216 (1917b).

Laboratory investigations of the acid and caustic soda procedures found in the literature cited above demonstrated certain processing difficulties which may make their commercial utilization impractical. Hydrochloric acid treatment dissolves the major portion of the magnesium in the Coal Creek serpentine, but the gel characteristics of the residual silica make the removal of the magnesium chloride quite difficult. Treatment with caustic soda solutions produces soluble silicates and insoluble magnesium compounds. Efficient removal of the highly adsorptive magnesium compounds from silicate solutions is even more difficult than the separation problems encountered in acid treatment. Treatment with CO₂ (carbonic acid) gave low yields, and its use appears to be uneconomical. The reported processes for decomposition of the serpentine with chlorine gas at high temperatures and with concentrated salt solutions other than the magnesium salts have not been evaluated.

TREATMENT OF RAW SERPENTINE WITH HYDROCHLORIC ACID

Effect of reaction time.—When unactivated serpentine is treated with hydrochloric acid, the magnesium and other metallic ions go into solution first and then the silica is converted to silicic acids and silica gels. As the attack on the silica increases, separation of the insoluble portion from the solution by filtration becomes increasingly difficult. If the hydrochloric acid is allowed to react in such a manner as to form a silica gel, separation of the magnesium chloride becomes impossible

by normal filtration methods. Acid concentration, reaction temperature, and size of the serpentine particles are some of the major factors which may influence the rate of magnesium solution and formation of silica gel. Crawford (1946) showed that the former two factors were of relatively minor importance so long as the mole ratio of acid to alkali was more than about 0.75 to 1.0.

Experimental data presented in Table 7 were obtained in the treatment of minus 60-mesh serpentine with 20 percent commercial hydrochloric acid at approximately 100° C. In each instance 100 grams of raw serpentine were allowed to react with 68 grams of acid (100% basis) (0.5 mole MgO to 1.05 mole HCl) for the indicated time and then filtered immediately in a 11-cm. Büchner funnel fitted with a #41 Whatman filter paper under a vacuum of 24 inches of mercury.

Table 7. Reaction of raw Coal Creek serpentine with hydrochloric acid.

Sample No.	Reaction time Minutes	Filtration time Minutes	Recovery of magnesium Percentage
1	5	1.83	85.5
2	10	2.67	90.1
3	15	2.83	91.8
4	20	3.07	92.1
5	25	3.25	91.2
6	30	3.59	91.8
7	60	5.10	93.2
8	120	9.00	93.2

These data show clearly that magnesium recovery, that is, percent of total magnesium obtained in the clear filtrate, reaches a maximum very rapidly, whereas silica gel formation, as indicated by longer filtration time, increases linearly with time of reaction. Optimum reaction time is about twenty minutes.

Effect of particle size.—Since any reaction of a liquid and a solid will be markedly affected by the exposed surface area of the solid, it was anticipated that both the amount of magnesium extracted and the time of filtration would vary with particle size. Data (Table 8) covering the results of acid treatment of crushed and sized serpentine show that, at least qualitatively, the reaction with acid is a function of particle size.

Table 8. Effect of particle size on magnesium extraction from Coal Creek serpentine by acid treatment using a standard reaction time of 15 minutes.

National Bureau of Standards sieve number		Filtration time Minutes	Recovery of magnesium Percentage
Through	On		
100		2.3	88.2
40	80	1.6	86.0
20	40	1.5	85.7
10	20	1.7	85.0
4	10	1.2	68.7

The amount of magnesium extracted does not drop markedly until the particle size is relatively large (+10 mesh). The filter time increases as the particle size gets smaller but, for this set of conditions, the change is not large. Fine-grinding (minus 100 mesh) does not increase the yield appreciably.

Siliceous residue.—In the treatment of Coal Creek serpentine the hydrochloric acid also extracts some materials other than magnesium from the rock. It is believed that those metals held in the molecular structure as replacements for the magnesium are extracted under the same conditions as the magnesium. Practically all the ferrous iron and nickel are removed. The iron and chromium which are held in the magnetite and chromite minerals are virtually unaffected and remain as a magnetic fraction in the siliceous residue. The siliceous residue, which is essentially an amorphous hydrous silica, is discussed at greater length on page 39. Its reactivity in the amorphous state suggests possible uses for this material.

SOLUBILITY OF ACTIVATED SERPENTINE

Serpentine which has been activated by heat treatment is more soluble, and, in general, is more readily attacked by acids. Brandenburg (1940) claims that MgO and MgSiO₃ are formed by the decomposition. X-ray studies discussed previously show that the activated rock gives no X-ray diffraction patterns; thus no identification of specific compounds is possible and all crystal structures present in the raw serpentine seem to be destroyed. It is believed that the increased solubility is due to destruction of the crystal structure and resultant disruption of the chemical bonds. Activated serpentine gives an alkaline test,

thus showing the presence of free magnesium oxide. Brandenburg (1940) reports that 30 percent of the total magnesium oxide is "free MgO" and can be dissolved by passing carbon dioxide into an aqueous suspension of the calcine. With Coal Creek serpentine approximately 25 percent extraction was obtained by this process.

Trials with other solvents showed that of the total magnesium oxide, 6 percent was removed by solution with sulfur dioxide, 9 percent was removed by solution with ammonium chloride-ammonium hydroxide reagent, and 18 percent was removed with ammonium chloride and carbon dioxide.

TREATMENT OF ACTIVATED SERPENTINE WITH HYDROCHLORIC ACID

The heat treatment not only increases the solubility or reactivity of the total magnesium, but there is evidence to show that it also makes the silica more easily attacked. A heat-treated serpentine sample, when acidified with concentrated hydrochloric acid, forms silicic acid gel very rapidly. The character of the gel depends on the amount and concentration of the acid and the heat treatment of the serpentine. An attempt was made to treat the activated serpentine with hydrochloric acid in such a manner so as to form a hard gel, similar to that obtained by neutralizing sodium silicate with acid. If such a gel could be formed, the solutes probably could be leached from it, leaving the silica gel as granules. The hardest gel produced, under the numerous conditions investigated, was a soft plastic mass not hard enough to handle easily. The best gel obtained was with completely activated serpentine mixed with enough 20-percent hydrochloric acid to give a 5 percent excess over the amount required to react with the total magnesium. When the acid is added to the dry serpentine and stirred slowly, the gel formation starts within a few minutes, and the gel reaches a maximum hardness in about an hour, at which time the heat from the reaction has dissipated. Upon leaching the gel, any filter medium used was soon plugged by the siliceous residue. However, a good recovery of magnesium was obtained with yields mostly above 90 percent. With activated

serpentine as well as with raw serpentine, the problem becomes a method of separating the soluble magnesium and other metal compounds from the insoluble or partially soluble silicates. Iron and nickel are also dissolved by acid treatment and may need to be removed. It has been noted that heat treatment causes some oxidation of iron in the activated serpentine.

TREATMENT OF ACTIVATED SERPENTINE WITH SALT SOLUTIONS

Extraction of "Free MgO" by Solution in Magnesium Sulfate

On the assumption that the magnesia contained in activated serpentine could be considered as "free MgO", the solubility of the magnesia in magnesium sulfate solutions was investigated. Feitknecht (1926) and Delyon (1938) show that magnesium oxide exhibits a marked solubility in aqueous solutions of such salts as magnesium chloride and magnesium sulfate. Thus if "free MgO" exists in activated serpentine it should be extractable in solutions of these magnesium salts. The use of activated serpentine as an alkaline material to remove excess acidity or to adjust the pH of magnesium sulfate solution in order to precipitate alkali-insoluble metals, such as nickel and iron, was also investigated.

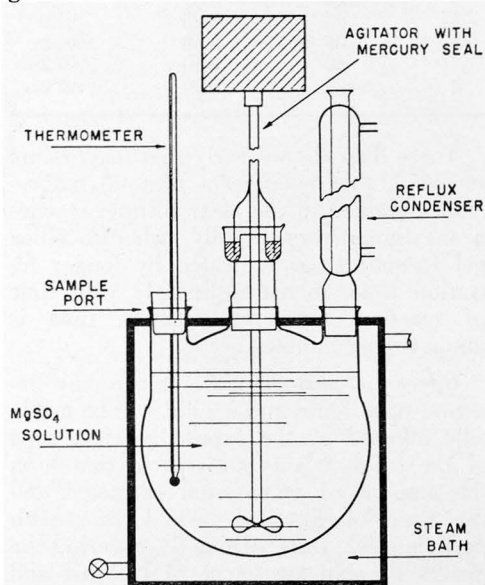


Fig. 14. Apparatus for treating activated serpentine with magnesium sulfate solution.

The method used was to introduce various weighed amounts of activated serpentine into well-agitated magnesium sulfate solutions of known strength kept at 100° C. The magnesium oxide content of the solution was determined by withdrawing an aliquot of the clear solution and titrating with standard tenth normal hydrochloric acid to the phenolphthalein end point. The apparatus used for this study is shown in figure 14.

Fifteen hundred ml. of magnesium sulfate solution were placed in the 2,000-ml. round bottom, 3-necked flask and heated to 100° C. in the steam bath; water loss was prevented by a condenser on one neck of the flask. The agitator was placed in the center neck and the serpentine was introduced and samples withdrawn from the third. Ten-cc. aliquots were used except in cases where the magnesium oxide content was very low; 25-cc. aliquots were used in such cases.

A glass tube filled with glass wool was placed over the pipet so that the aliquot drawn was free from the serpentine. The amount of alkaline material in the aliquot as measured by the titration was considered to be MgO. In each instance the

initial solution gave no test for alkalinity. This system of measuring MgO content was the same as that used by Delyon (1938), and the results obtained confirmed her observations that the magnesium oxide first went into solution and then reprecipitated. The total quantity of soluble magnesia removed from the serpentine is indicated by the maximum quantity of magnesium oxide shown by the titration. The serpentine used was ground to pass a 100-mesh screen, was activated 3 hours at 650° C., and had an activity number between 2 and 4 according to the evaluation system previously described. Five-gram samples of the activated serpentine were used.

Data covering the solubility of the magnesium oxide of activated Coal Creek serpentine in magnesium sulfate solutions of various concentrations are plotted in figure 15. Though the maximum magnesium oxide concentration obtained was much less than that obtained by Delyon (1938) with pure materials, the same characteristic decrease after reaching a maximum was observed. Delyon attributes this decrease to precipitation of some of the dissolved magnesia as basic magnesium sulfate. Since a 5-gram sample of the acti-

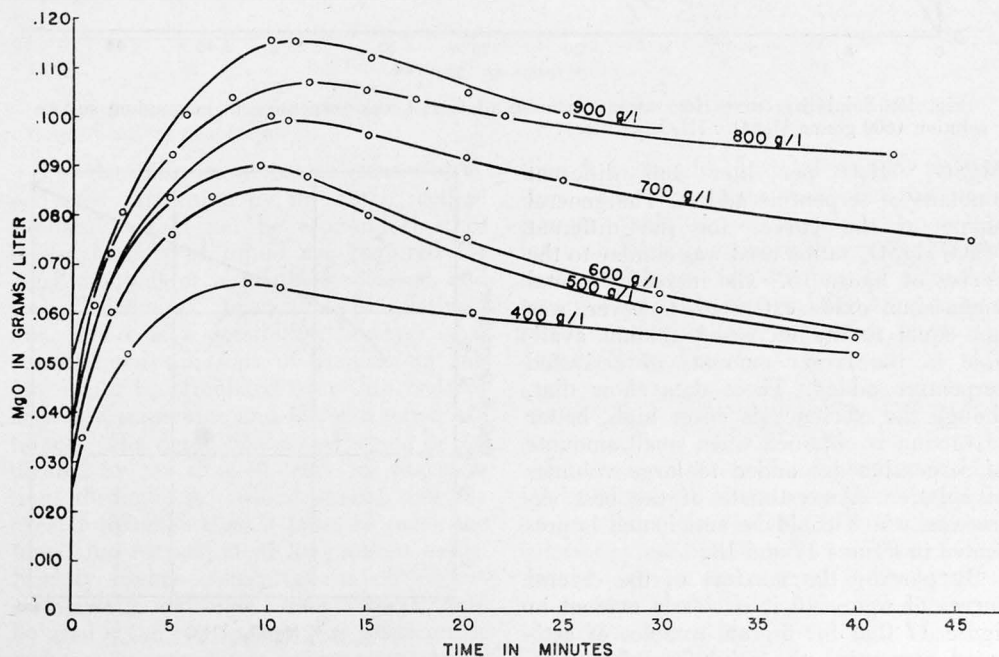


Fig. 15. Solubilities of magnesium oxide from activated Coal Creek serpentine in magnesium sulfate solutions. Parameters used are concentrations of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in grams per liter.

vated serpentine contained more than 2 grams of magnesium oxide, it is evident that only a small fraction of this total was dissolved.

In figure 16 are shown the data resulting from a slight modification of the solubility studies in which the concentration of the solution was held constant at 600 grams

upward from 500 grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter.

The solid curves of figure 18 show the maximum extraction obtained as well as the percent of total magnesium oxide dissolved in magnesium sulfate solutions of 600 grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter for increasing MgO/MgSO_4 ratios. Predicted

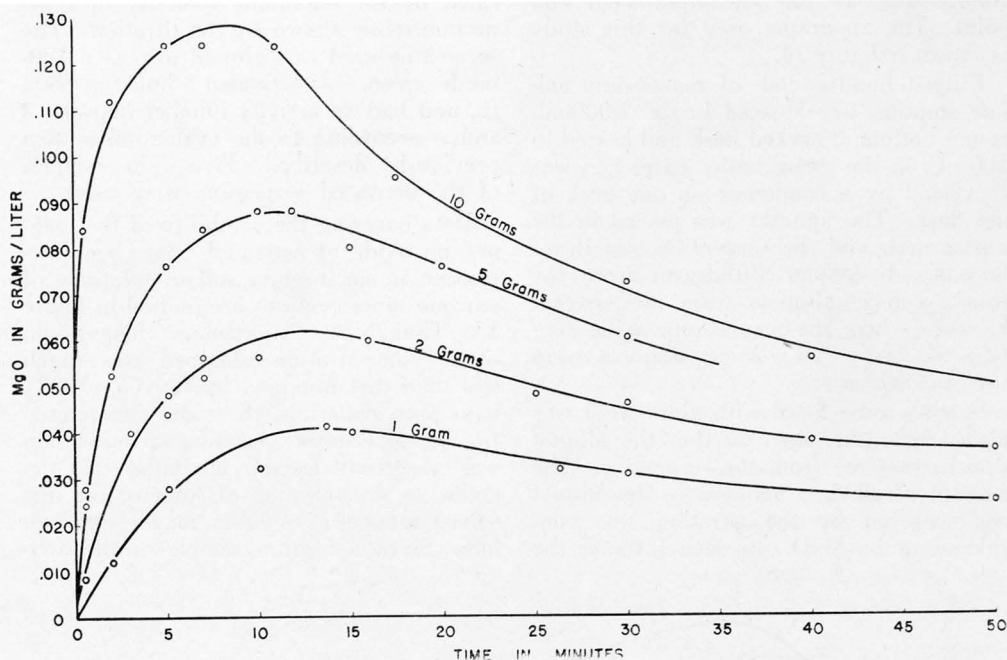


Fig. 16. Solubility curves for varying amounts of Coal Creek serpentine in magnesium sulfate solution (600 grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter).

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter and different amounts of serpentine added. The general shape of the curves for the different MgO/MgSO_4 ratios used was similar to the curves of figure 15. The increase in total magnesium oxide extracted, however, was not equal to the increased amount available in the larger amounts of activated serpentine added. These data show that, though the efficiency is never high, better extraction is obtained when small amounts of serpentine are added to large volumes of solution. An estimate of the best extraction which could be anticipated is presented in figures 17 and 18.

By plotting the maxima of the several curves of figure 15 it is clearly evident in figure 17 that for 5-gram samples of activated serpentine the solubility of magnesium oxide increases linearly for magnesium sulfate in concentrations ranging

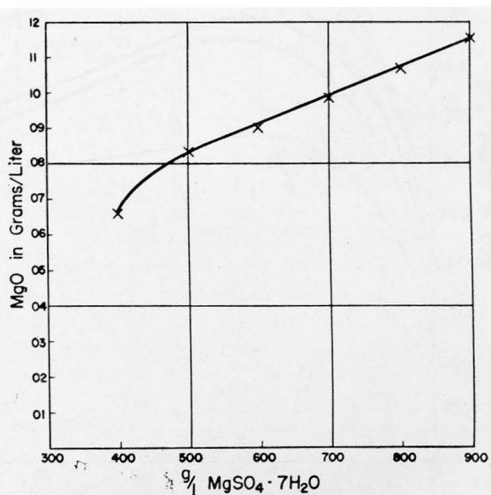


Fig. 17. Curve showing solubility of Coal Creek serpentine in magnesium sulfate solutions; maxima plotted from figure 15.

solubility data to be expected for magnesium sulfate solutions of 900 grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter are plotted by dashed lines in the same figure. These latter curves indicate quite clearly that very poor recovery of magnesium oxide from activated serpentine can be expected even where using hot solutions of magnesium sulfate of even near-maximum concentrations.

per liter and since the solubility of MgO could be expected to decrease at higher temperatures.

Because the solutions were basic, no iron or nickel was dissolved. The results also show quantitatively, as was indicated by qualitative observations, that in raising the pH of magnesium solutions with activated serpentine it is more effective to add the serpentine in small increments

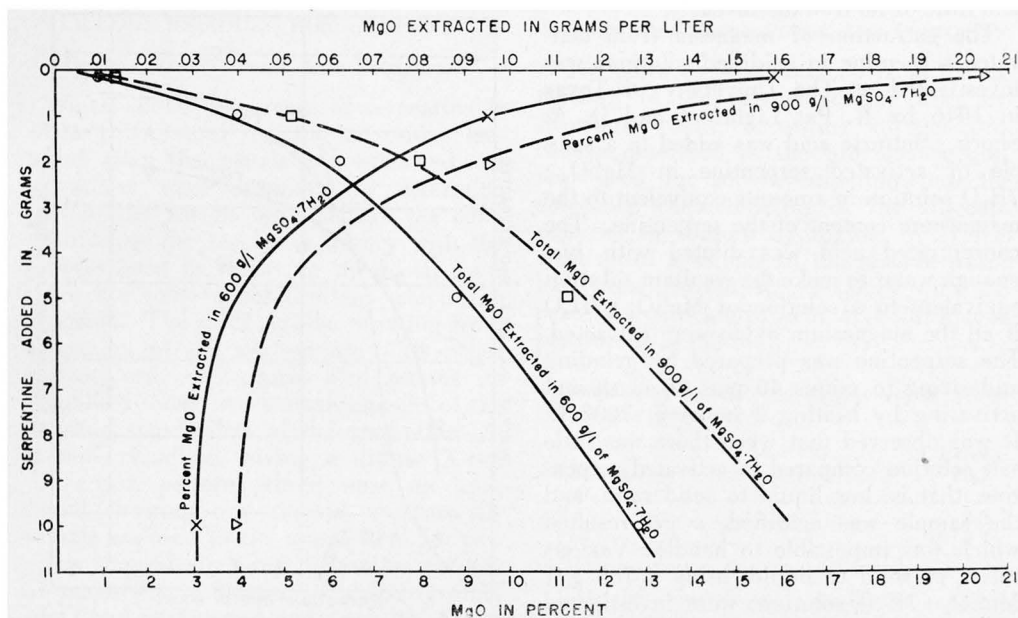


Fig. 18. Recovery curves for magnesia from Coal Creek serpentine in magnesium sulfate solutions of various concentrations.

The data also show that an extraction of activated serpentine by the batch method probably would not be economical since large amounts of liquid are required for small amounts of serpentine processed, and the efficiency of extraction is relatively low. There is a possibility, however, that concentrated solutions of magnesium sulfate could be circulated over thin beds of activated serpentine and fair extraction obtained. The depth of the bed would be indicated by the time of travel of the solution through it, which should not be greater than the time it takes to reach the maximum extraction of magnesium oxide. Slightly higher concentrations of magnesium sulfate and higher temperatures could be used if the extractions were made under pressure but not much improvement could be expected of these since the limiting solubility of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is about 900 grams

than it is to add the total amount at one time. The above data show that the magnesium oxide is not dissolved from the large additions but more is extracted from small additions. The amounts of extracted magnesium oxide expected for a given serpentine addition are indicated from the data in figure 18.

Solubility of MgO in Acidified Magnesium Sulfate Solutions

Since the quantity of soluble magnesium oxide decreased in a relatively short time on extraction in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, solutions acidified with sulfuric acid should increase the amount of magnesium oxide dissolved. One gram of activated serpentine was placed in 600 g/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution which was heated at 100°C . and agitated as in the previous experiments; enough normal sulfuric acid was

added to be equivalent to the magnesia in the serpentine. The calcined serpentine was added and the solution filtered at the end of 20 minutes. Filtration was very rapid and the solution gave no test for iron. Analysis of the extracted serpentine showed that 66 percent of the total magnesium oxide had been removed. In this manner a better recovery of the magnesia could be effected, filtration time decreased, and little or no iron dissolved.

The extraction of magnesia from activated serpentine in acidified solutions was investigated at The University of Texas in 1946 by R. Pat Lightfoot and D. A. Shock. Sulfuric acid was added to a sample of activated serpentine in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution in amounts equivalent to the magnesium content of the serpentine. The concentrated acid was diluted with just enough water to make the resultant solution equivalent to a solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ if all the magnesium oxide were extracted. The serpentine was prepared by grinding and sizing to minus 40 plus 80 mesh and activating by heating 3 hours at 700°C . It was observed that when there was little salt solution compared to activated serpentine, that is, low liquid to solid ratio, and the sample was acidified, a gel resulted which was impossible to handle. Various ratios of solid to liquid, using a 760 g/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution, were investigated to find which ratio is best, and the results are shown in Table 9.

In order to keep the production of gelatinous silica at a low point so the filter rate would not be too greatly reduced, a solids-to-liquid ratio of about 50 g/l was maintained.

The amount of magnesium which could be extracted in this manner, related to filter time of the sample, was studied by reacting for various lengths of time 10 grams of activated serpentine in 200 cc.

of 760 g/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 100°C . with an amount of 48 percent H_2SO_4 equivalent to the magnesium. Reaction was carried out in an open beaker, with mild agitation and acid added within the first 5 minutes of the reaction period. The slurry was filtered in a Büchner funnel under constant vacuum and the filter time noted. The residue was dried and analyzed for the remaining magnesium content. Figure 19

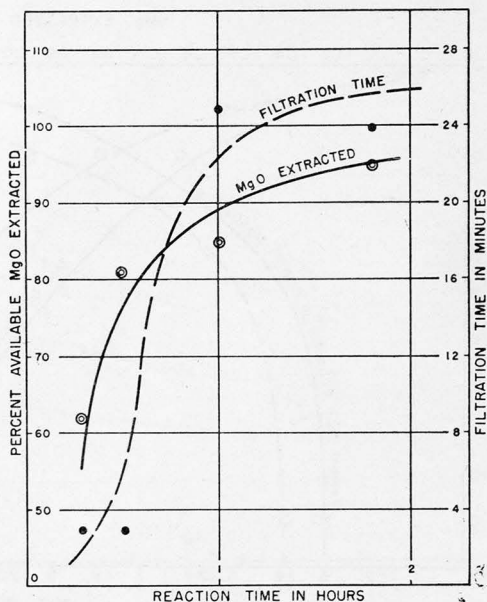


Fig. 19. Rate of magnesia extraction from Coal Creek serpentine in 760 g/l magnesium sulfate solution and sulfuric acid and filtration rate of solution.

shows the efficiency of Mg extraction and comparable filter time for minus 40 plus 80 mesh serpentine in batches which were reacted for various lengths of time. The curves show that after the rate of Mg solution drops off, the filter rate increases rapidly. This limits the economical extraction of magnesium oxide as was found

Table 9. Ratios of activated Coal Creek serpentine to liquid for extraction of magnesia in magnesium sulfate-sulfuric acid solutions.

Activated serpentine in grams Minus 40 plus 80 mesh	Volume in cc. of 760 g/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ plus H_2SO_4	Observations
10	18.6	Gels solidify immediately on acid addition
10	37.2	Gels solidify in 10 minutes after acid addition
10	74.4	Filters very slowly; some gelation
10	186	Filters rapidly 10 minutes after acid addition

to be the case in other extraction procedures. According to these data a yield of 80 to 85 percent is to be expected with good filter rate. The extracted solutions showed no iron to be present.

In consideration of these results it seems possible that a one-step process of reasonable efficiency for making magnesium sulfate from activated serpentine may be feasible.

SILICEOUS RESIDUE FROM SERPENTINE

RESIDUE AFTER STRONG ACID EXTRACTION

Since about 40 percent of serpentine is silica (SiO_2) and remains as residue material after the metals are extracted, its properties were examined to determine possibilities for its use. Though the composition of the residue will vary with the process used in removing the metal ions, there are some generalizations which can be made. The silica residue resulting from extraction of the ground ore with either hydrochloric or sulfuric acid retains its combined water and a small amount of the cationic constituents of the serpentine. It is non-crystalline, giving a diffuse X-ray diffraction pattern; there were no lines found showing any silicate structure. A sample exposed to the atmosphere for two years showed an X-ray diffraction pattern of magnesite, indicating that the residual MgO had carbonated and crystallized, but the complete absence of diffraction lines attributable to crystalline silica or silicate minerals showed conclusively that the former remained in the amorphous state.

Much of the usual residue after acid treatment is a gray-white powder which is easily pulverized. The larger pieces crumble easily and do not maintain their granular character as well as commercial granular silica gels. The apparent density (1.5 g/cc for extracted ore which had been ground to pass a 100-mesh screen) is high, especially if compared to silica gels available on the market. Hydrochloric acid extraction removes more of the colored ions, iron and nickel, and gives a whiter residue than extraction with sulfuric acid. The general properties are otherwise similar.

Siliceous residues resulting from extraction processes which use activated serpentine are also non-crystalline but they do not contain combined water. In other

words, exposure to an aqueous system at process temperatures is not sufficient to allow the water to recombine in the amount that was driven off by the activation treatment. These residues contain more iron, much of which is in ferric form as a result of oxidation during heat treatment. These activated serpentine residues are generally less reactive than those obtained by acid extraction of the raw ore.

RESIDUE FROM HYDROCHLORIC ACID EXTRACTION

The silica residue obtained from the extraction of the raw serpentine with hydrochloric acid, according to the procedure described in the previous section, was used for an investigation into the solubility characteristics of the siliceous material in sodium hydroxide. A typical analysis of a sample of the residue which had been reacted for 2 hours with 20-percent hydrochloric acid at boiling temperature is as follows:

Composition of siliceous residue (after hydrochloric acid extraction).

	Percent
Ignition loss (combined H_2O)	18.7
SiO_2	76.6
R_2O_3	3.8
Fe_2O_3	0.2
MgO	1.5

R_2O_3 by spectroscopic qualitative analysis showed chromium as a major component with iron and aluminum next in concentration.

SOLUBILITY IN NaOH SOLUTIONS

The silica residue, being finely divided and non-crystalline, exhibits a greater reactivity than any of the crystalline types with which it was compared. It was found to be readily soluble in sodium hydroxide solutions of various concentrations. Solution was effected by adding the silica residue to known concentrations of sodium hydroxide at constant temperature. Moderate stirring was used. The solution and silica were reacted for a definite time and the resulting solution analyzed for SiO_2 . Solubility was considered to be the amount of silica in solution as determined by analysis. The effect of time on the solubility of a 2.5 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio mixture (10 percent NaOH concentration) held at 100°C . is shown in Table 10. The difference between batches A and C was in their particle size, which is given in Table 14.

Table 10. Effect of reaction time on solubility of silica residue at 100° C.

Reaction time	Percent of total silica dissolved
Batch A*	
10 minutes	96
15 "	94
20 "	93
25 "	100
30 "	97
1 hour	101
1.5 "	100
2 "	98
Batch C	
5 minutes	89
10 "	95
15 "	91
20 "	95
25 "	91
30 "	93

*See Table 14 for characteristics of batches A and C.

These results, while somewhat variable, indicate that for 2.5 SiO₂/Na₂O ratio at 100° C. the reaction is very rapid, being essentially complete in 10 minutes. At room temperature (30° C.) the reaction was considerably slower, as shown by Table 11.

Table 11. Effect of reaction time on solubility of silica residue at 30° C.

Reaction time Hours	Percent silica dissolved
1.5	79
2.5	83
4.5	86
6.0	84
8.0	99

EFFECT OF SiO₂/Na₂O RATIO ON SOLUBILITY

In order to determine the solubility of the silica when different amounts of sodium hydroxide were used, a series of tests was made by adding various amounts of silica residue to a given volume of 10 percent NaOH solution. The sample was agitated at 100° C. for the time shown in Table 12. The filtrate was analyzed for Na₂O and SiO₂ content and the rate and yield thus determined.

These results would indicate that below a ratio of 4 the solubility is independent of the SiO₂/Na₂O ratio, but above 4 the solubility decreases as the ratio increases.

The solution ratio seems to reach a maximum value at 5.1–5.4 in solution. It is possible to remove some of the undissolved magnesium oxide and ferric oxide by settling. Experiments on settling time show that as the SiO₂/Na₂O ratio increases, the solutions are more viscous and become increasingly difficult to clarify. Increase in reaction time was found to decrease the difficulty of clarification.

Table 12. Effect of SiO₂/Na₂O ratio on solubility of silica residue.

SiO ₂ /Na ₂ O calculated	SiO ₂ /Na ₂ O determined in solution	Reaction time Hours	Percent total SiO ₂ dissolved
2.0	1.96	2	98
2.5	2.32	2	93
3.0	2.94	2	98
3.5	3.43	2	98
4.0	3.6	2	90
2.0	1.94	0.25	97
2.5	2.42	0.25	97
3.0	2.91	0.25	97
3.5	3.40	0.25	97
4.0	3.88	0.25	98
5.0	4.20	0.25	84
6.0	5.10	0.25	85
7.0	5.4	0.25	77

EFFECT OF NaOH CONCENTRATION ON SOLUBILITY

Three concentrations of sodium hydroxide were used to determine any effect of concentration change on solubility. The results shown in Table 13 indicate that there is little change in solubility in these ranges.

Table 13. Effect of sodium hydroxide concentration on solubility of silica residue.

NaOH concentration Percent	Reaction time Hours	Specific gravity	Percent yield, SiO ₂ dissolved
10	2	1.185	97
15	2	1.195	98
20	2	1.193	95

EFFECT OF INITIAL PARTICLE SIZE ON SOLUBILITY

Since solubility characteristics can be changed by the particle size, three batches of silica residue were sized and samples from the batches were then dissolved in 10-percent sodium hydroxide. Screen analyses of the batches are shown in Table 14.

Table 14. Screen analyses of silica residue.

National Bureau of Standards sieve number		Batch A	Batch C	Batch D
Through	On			
10	20	4.1	0.0	0.0
20	40	12.4	1.5	0.0
40	60	7.7	9.2	2.0
60	100	14.1	25.4	19.0
100		61.5	55.6	62.9

Percent silica dissolved from the batches
above in 2.5 SiO₂/Na₂O ratio 10-percent

NaOH solution at 100° C. is shown in
Table 15 which indicates little effect of
particle size on solubility over this range.

Table 15. Effect of particle size on solubility
of silica residue.

Reaction time Minutes	Yield, Batch A	Yield, Batch D	Yield, Batch C
10	96	95	—
15	94	91	93
30	97	93	95

PART 4

REVIEW OF THE POSSIBLE INDUSTRIAL USES OF SERPENTINE

W. A. Cunningham

The possible sources of magnesium available in the southwestern United States are listed in Table 16. Of the ores available in any quantity, serpentine has the highest magnesium content since neither brucite nor magnesite is present in significant amounts. This fact alone, however, does not necessarily imply that this mineral is the best raw material from which magnesium or magnesium compounds might be produced commercially. Indeed, the fact that magnesium metal is being produced from sea water, which has the lowest magnesium content of all the sources listed in Table 16, is strong evidence that other factors have a greater influence on commercial utilization than does the amount of magnesium present in an ore or mineral.

In considering the possible industrial uses of any raw material, it must be kept very clearly in mind that the mere availability of large quantities of that material, even if it contains a relatively high content of potentially valuable elements or compounds, does not mean that it can be processed economically. This is particularly true of a mineral as complex as serpentine. Hence, in the following pages some of the other factors will be presented,

but no attempt will be made to discuss all such factors or to draw specific conclusions as to whether or not the use of serpentine for certain specific purposes is economically feasible. Changes in demand or advances in technology can alter completely the present status.

Since little serpentine is now being used commercially, the only basis for uses suggested are the laboratory data reported herein or data in the literature. None has been studied in sufficient detail to insure its success, either technically or economically.

SERPENTINE AS A SOURCE OF MAGNESIUM COMPOUNDS

MAGNESIUM CHLORIDE FOR MAGNESIUM METAL MANUFACTURE

The rapid expansion, and attendant publicity, of the magnesium metal industry during the past decade quite naturally raises a question about the possibilities of the use of serpentine as a raw material. The most widely used process for making metallic magnesium involves, basically, the electrolysis of a fused salt mixture containing approximately 50 percent magnesium chloride. Hence, the possible use of ser-

Table 16. Possible sources of magnesium available in southwestern United States.

Source	Composition	Percent magnesium
ROCKS		
Brucite	$Mg(OH)_2$	42
Magnesite	$MgCO_3$	29
Serpentine	$H_4Mg_3Si_2O_{10}$	26
Olivine	$MgSiO_4$	21
Dolomite	$MgCO_3 \cdot CaCO_3$	13
SALTS		
Kieserite	$MgSO_4 \cdot H_2O$	17
Langbeinite	$2MgSO_4 \cdot K_2SO_4$	11
Kainite	$MgSO_4 \cdot KCl \cdot 3H_2O$	10
Carnallite	$MgCl_2 \cdot KCl \cdot 6H_2O$	9
Polyhalite	$2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$	4
BRINES		
West Texas brines	$NaCl$; KCl ; $MgSO_4$; $CaSO_4$	1
Michigan brines*	$MgCl_2$; $CaCl_2$; $NaCl$	0.8
Great Salt Lake*	$MgCl_2$; $NaCl$; etc.	0.6
Sea water	$MgCl_2$; $NaCl$; etc.	0.13

*Listed for comparison only.

pentine for this purpose becomes essentially a process for the efficient and economical manufacture of magnesium chloride.

During the war the research staff of the International Minerals and Chemical Corporation, which operated a magnesium plant near Austin, Texas, in which the fused salt electrolytic process was used, made a rather careful study of the possibilities of the use of serpentine as a raw material for its process. The primary effort was expended in an attempt to develop an economical process for the production of magnesium chloride as a possible replacement of the company's process in which dolomite was used as a basic raw material.

Belik (1939) describes a process of manufacturing $MgCl_2$ from serpentine by reaction with chlorine and cadmium metal at $1,000^\circ C$. A relatively simple process of controlled reaction of HCl with serpentine was described by Butt et al. (1946) which promised to be as economical as the dolomite process in use at Austin. The serpentine process proposed for use, covered by the disclosures in the patent, depended on the solubility behavior of serpentine in 20-percent HCl . These data have been presented previously (p. 39) and will not be discussed in detail here. Two general processes were proposed using this method. One process required the solution of the cations in hot 20-percent HCl under controlled conditions, oxidation of the ferrous to ferric iron, treatment with small amounts of activated serpentine to precipitate the iron, filtration and then dehydration to $MgCl_2$ cell feed. The second process differed from the first only in the use of $Mg(OH)_2$ from sea water to precipitate the iron. Using the known costs of the dolomite process, a comparative cost per ton of cell feed was estimated as shown in Table 17.

Table 17. Comparative cost of cell feed from dolomite and serpentine.

Process	Needed to produce 150 tons cell feed	Cost per ton as 34% liquor
Dolomite	300 tons dolomite	\$14.82
Serpentine, I	163 tons serpentine	9.65
Serpentine, II	131 tons serpentine	11.93

It is apparent that either of the serpentine processes had the possibility of making savings over the dolomite process in use, with the first serpentine process making a substantial saving, though disposal of the siliceous residue would have presented a major problem.

The cost values presented are peculiar to the conditions and manufacturing process used at the Austin plant and are of value for comparison only. It is important in that if the data on both the dolomite process and serpentine process had been available soon enough, it is probable that the process chosen for use at the Austin plant would have been to use serpentine for raw material rather than dolomite. Should another such emergency demand arise, this source of magnesium should not be ignored.

If the fundamental data on the chemistry of the serpentine minerals are sufficiently advanced, it is possible that other more economical processes can be developed for the manufacture of magnesium metal.

MAGNESIUM SULFATE (EPSOM SALTS) MANUFACTURE

From the data developed on the extraction of magnesium from serpentine by sulfuric acid, it is evident that it is technically feasible to make magnesium sulfate and Epsom salts in that manner. Whether or not the processes would be economically attractive has not been ascertained.

From the acid extraction data it seems that either of two methods may be employed. The first method requires the extraction of magnesium from the raw serpentine for a limited time, filtration, oxidation of the iron, precipitation of the iron with magnesium oxide or activated serpentine, separation of the ferric hydroxide, concentration, and crystallization of the magnesium sulfate. The second method involves extraction of the activated serpentine with sulfuric acid in concentrated magnesium sulfate solutions, filtration, concentration, and crystallization. While the second process appears to be the more direct, it requires the activation of all the ore whereas the first process uses largely raw serpentine. Some Epsom salts is being made from serpentine by acid extraction in Georgia; this is the only plant now known to be utilizing serpentine as a

raw material, and the quantity produced is small.

W. H. MacIntire (1942) patented a process whereby a fertilizer grade of magnesium sulfate can be produced by mixing ground serpentine and relatively concentrated sulfuric acid (77 percent) together in a mixing device similar to that used to produce rock phosphate. The slurry of acid and serpentine reacts and gives off heat enough to dry the mass, producing a granular material high in soluble magnesium.

One of the major costs in producing magnesium sulfate by sulfuric acid extraction of serpentine is the cost of sulfuric acid. A cheap acid is prerequisite to an economical process. The cost could be considerably reduced if the magnesium sulfate could be produced from elemental sulfur or iron pyrite.

Brandenburg (1940) refers to a process for manufacturing magnesium sulfate by heating a ground mixture of iron pyrite and serpentine; however, no data are given concerning efficiency of extraction or economics of the process. The major amount of the Epsom salts now produced in this country is made by a process in which magnesium hydroxide, made by adding lime to a brine, is reacted with sulfur dioxide, made by burning sulfur or iron pyrite, and the sulfate produced by introduction of steam and air. A method of producing magnesium sulfate directly from serpentine and sulfur could cut the production cost to such a point that the utilization of serpentine might be very attractive.

MAGNESIUM OXIDE AND OTHER CHEMICALS

Numerous patents disclose methods for converting serpentine into salts and compounds which can be processed to make other compounds. Samuel Peacock holds two patents on processes utilizing serpentine. One (1917a) claims the production of magnesium oxide and soluble silicates by solution of serpentine in sodium hydroxide. The other (1917b) claims the production of magnesium chloride by extraction of serpentine in concentrated salt solutions of calcium chloride and production of magnesium oxide or other chemicals by base exchange or precipitation. B. A. Peacock's patent (1919)

claims that serpentine can be mixed with potassium-bearing silicates, such as the feldspars, and heated with concentrated sulfuric acid to produce solutions of potassium and magnesium sulfate. These are separated by the usual procedures of separation such as precipitation by potassium hydroxide or carbonate and filtration of the soluble potassium salts. Norwegian patents 37,109 and 37,784 (Aktieselskapet de Norske Saltverker, 1923a-b) disclose methods of obtaining salts, particularly nitrates, and the silica in filterable form by addition of the acid to strong salt solutions. Oganessian (1938) claims that magnesium is extracted from serpentine by the ammonium chloride liquor such as is obtained from the Solvay process. Jackson's patent (1918) claims that serpentine treated with sodium hydroxide under specified conditions yields an acid-soluble magnesium silicate which can be converted into the desired salts. Terpugov and Tiktina (1938) describe a process of acid solution of serpentine and precipitation of magnesium as the basic carbonate which is calcined to yield MgO. Brandenburg's patent (1944) and article (1940) claim that magnesium can be extracted from the activated rock by carbon dioxide forming soluble magnesium bicarbonate. Magnesium oxide is produced by heating the bicarbonate solution, precipitating the basic salt, filtering the insoluble precipitate, and calcining to the oxide.

So far as is known there is at present no production of oxides or other miscellaneous salts in this country which utilizes serpentine as a raw material. The competitive production of magnesia from magnesite, brucite, or possibly dolomite for such purposes as insulation and refractories would limit seriously the economic production of magnesia from serpentine which would require numerous chemical steps. It is believed that only in cases where a peculiar set of processing conditions was present would the production of magnesia be economical.

SILICATE COMPOUNDS FROM SILICA RESIDUES

The silicate portion of serpentine has been considered the least soluble and therefore the waste product from the magnesium extraction processes. Samuel Pea-

cock's patent (1917a) describes the formation of a soluble silicate in the process, though its major emphasis is on the production of the magnesia, not the soluble silicate. Since the silica content represents the major constituent in serpentine, the possibilities of utilizing this portion must be given serious consideration in any process requiring chemical decomposition of the mineral.

SODIUM SILICATE MANUFACTURE FROM SILICA RESIDUE

The insoluble residue left from the hydrochloric acid extraction of raw serpentine in the production of magnesium chloride was found to be soluble in sodium hydroxide. The solution of this silica residue showed that the formation of sodium silicate of technical grade was easily accomplished. Data (p. 40) show that practically all the silica dissolves (95 percent solution) and that the solutions can be made in numerous $\text{Na}_2\text{O}/\text{SiO}_2$ ratios. Removal of the last traces of magnesia is difficult, but iron and the heavy metals are separated easily. Chromates are formed if the magnetic portion (magnetite and chromite) is not removed from the residue before solution in caustic. The data indicate that production of sodium silicate using the silica residue and caustic soda should give commercial grades of sodium silicate.

SILICA GEL MANUFACTURE FROM SILICA RESIDUE

From the production of sodium silicate it is a simple step to the production of silica gel by neutralization with acid and leaching the gel formed until the soluble salt is removed, then drying, and activating. Silica gel was made from serpentine in this manner for a time during World War II at the Georgia plant which makes magnesium sulfate.

OTHER USES OF SILICA RESIDUE

Terpugov and Portugalova (1938) describe a process for using the silica acid waste from serpentine extraction as an adsorbent for decolorizing mineral and vegetable oils. It is reasonable to expect the siliceous residue to have surface-active properties and, in fact, to be quite similar to silica gel. Dehydration should further

increase this activity since the loss of the combined water would increase the active area.

The fact that the silica residue after acid extraction is amorphous, reactive, and fairly pure, should give a combination of properties which would be valuable as a starting point for making silicon compounds. Winding (1944 a-d) gives several silicate compositions which are claimed to have superior catalytic and adsorptive properties. With the increasing importance of the organic silicates, the organic compounds should not be overlooked as possible end products.

THE USE OF SERPENTINE IN FERTILIZERS

Agricultural research has shown that magnesium is one of the elements which should be included in fertilizing many soils. The necessity that it be added in an available form is apparent; however, most soluble magnesium compounds which can be used are so soluble that they are rapidly dissolved and leach out of the soil and are carried away by the surface water. Untreated serpentine has been evaluated for its comparative value as a magnesium source by Vlasjuk (1940) and Lea and Smith (1938) who found that little of the magnesium is in available form. However, when treated with acid along with phosphate rock to make a serpentine superphosphate, better results are obtained (Elliott, 1940; Elliott and Lynch, 1941; Askew and Stanton, 1942). Elliott and Lynch (1941) claim that the serpentine superphosphate gives better performance than superphosphate alone. Recent work reported to the Fertilizer Division at the 112th Meeting of the American Chemical Society shows that serpentine additions increase the available magnesium in phosphate fertilizers as well as or better than olivine or magnesite. The magnesium salts formed by this treatment have a limited solubility which permits sufficient magnesium to be liberated for plant use without being soluble enough to be rapidly dissolved away by the surface water.

The heat-treated activated serpentine should find some use in soil conditioning as a treatment for acid soils. The experiments on activation have shown that proper treatment will liberate magnesia. Sam-

ples tested by the American Association of Official Agricultural Chemists' method for determining active magnesia in burned magnesite show that properly activated serpentine contains available magnesia. In soil areas requiring magnesium additions where magnesite is unavailable, serpentine may fill an important need.

MISCELLANEOUS USES OF SERPENTINE

Olivine-forsterite refractories.—There are numerous references in the literature on the use of olivine and forsterite in the manufacture of refractories. Since it is known that the Coal Creek serpentine gives olivine on heating, the use of serpentine for this type of refractory seems possible. Pieper (1937) discusses the use of serpentine in German refractory materials. Goldschmidt (1938), Malquori, Sollazzo, and Giannone (1938), and Tsynkina (1938) review the use of olivine-forsterite refractories. Harvey and Birch (1935) have patented a refractory using forsterite and magnesia. The use of this type of refractory is for copper roasting, open-hearth steel furnaces, and ceramic kilns. With the growth of the clay-product industry in the Southwest, some use for serpentine may be found in the manufacture of refractories.

Surface-active material.—Laboratory work has shown that on controlled heating the crystal structure of serpentine is destroyed and the resultant material becomes relatively active chemically. Though laboratory test data have shown conflicting results, the possibilities of obtaining a good basic adsorbent by calcining serpentine must not be overlooked.

Allied with the surface-active properties of adsorption are the properties which make a material a suitable catalyst. No

laboratory data have been gathered on the possibility of using surface-active serpentine in catalytic reactions. Eisenack (1939) states that serpentine has a catalytic action on compounds with amine groups and phenol, giving rise to colored dyes. Other reactions may be found in which serpentine, raw or activated, would serve as a catalyst.

Ion exchange minerals.—Like many complex silicates, serpentine exhibits some ion exchange properties. Data from the literature furnish no indication that the raw serpentine possesses very attractive properties for use in ion exchange. Kappen and Fischer (1928) studied the exchange capacity of numerous natural silicates which included serpentine, and Ginzburg and Ponomarev (1939) claimed that nickel can be adsorbed and replaced by serpentine and other hydrosilicates. Since the extraction of the magnesium from the raw serpentine by a strong mineral acid may be considered an ion exchange, it is possible that the siliceous residue would exhibit some useful ion exchange capacity. There are no laboratory data to substantiate this hypothesis, however.

Use as rock.—The principal discussion of the uses for serpentine has been confined to its use as a raw material for some chemical product or in some considerably altered form. This was due to the fact that so little market exists for the material as the native rock. Some rock is used for green-colored chips for terrazzo floors, and there is a limited market for finely ground serpentine. Bradley (1937) mentions its use as a weighting and flattening agent in the paint industry. Bowles (1944) lists a small consumption as ground rock. This market is small and products have little value to support a continuous operation.

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- Crystal structure from X-ray examination—
Anderson and Clark (1929); Boldyrev, Mikheev, Kovalev, and Dubinina (1939); Bragg (1937); Warren and Bragg (1930); Caillière (1936); Haraldsen (1928); Hargreaves and Taylor (1946); Hendricks (1942); Kurnakov and Chernukh (1926); Selfridge (1936); Warren and Bragg (1930)
- Deposits in central Texas—
Baker (1935); Barnes (1940, 1943, 1945a, 1945b); Barnes, Dawson, and Parkinson (1947); Comstock (1890, 1891); Paige (1911, 1912); Romberg and Barnes (1949); Schoch (1920); Sellards (1933); Udden, Baker, and Böse (1919)
- Genesis—
Bowen (1947); Bowles (1944); Chawner (1934); Hess (1939); Jander and Wuhler (1938); Lonsdale (1927)
- Heat decomposition—
Brandenburg (1940, 1944); Caillière (1936); Haraldsen (1928); Rudneva (1939)
- Separation of magnetic fraction—
Hills (1946)
- Synthesis—
Bowles (1944); Brandenberger, Epprecht, and Niggli (1947); Noll (1944a, 1944b)
- Thermal analysis—
Caillière (1936); Efremov (1940); Ivanova (1941); Kurnakov and Chernukh (1926)
- Use of serpentine—
Adsorption and catalytic agent—
Terpugov and Portugalova (1938)
- Fertilizer ingredient—
Askew and Stanton (1942); Elliott (1940); Elliott and Lynch (1941); Lea and Smith (1938); Vlasyuk (1940)
- Magnesium chloride—
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- Magnesium sulfate—
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- Refractories—
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- Silica residue—
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- Composition—
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